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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 33, No. 2, August 1965

THE EXTRACTION OF ELEMENTS WITH CYCLIC SOLVENTS AND ITS APPLICATION TO GEOCHEMICAL ANALYSIS

The extraction of the elements Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb and Bi into the solvents cyclohexanone, cyclohexanol, and cyclohexane from hydrochloric acid solutions, has been studied. Cyclohexanone is a more efficient but less selective extracting agent than cyclohexanol while cyclohexane has little extracting power. Solvent extraction of hydrochloric acid solutions of materials of geochemical interest into cyclohexanone has been used to enrich trace elements prior to spectrochemical analysis.

C. R. Boswell and R. R. Brooks,
Anal. Chim. Acta, 33 (1965) 117–122

NEUTRON ACTIVATION ANALYSIS OF COPPER IN BISMUTH BY γ, γ-COINCIDENCE MEASUREMENT

Copper was determined non-destructively by neutron activation analysis in high-purity bismuth down to concentrations of 30 p.p.b. By using γ, γ-coincidence counting of the annihilation photons of ^{64}Cu, interferences from the bremsstrahlung of the matrix could be completely suppressed, together with the interferences due to the induced γ-activities of other impurities as Zn, Cd, Au, Ag, Sb and As.

The accuracy of the method was tested by spectrophotometry and by destructive activation analysis. The technique was applied to the analysis of a high-purity bismuth rod.

J. I. Kim, A. Speecke and J. Hoste,
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THE DETERMINATION OF NIOBIUM IN STEEL BY NEUTRON ACTIVATION

A method is described for determination of niobium in steels by neutron activation analysis. It is applicable to samples containing down to 3 μg of niobium; but this sensitivity may be improved by a factor of 10 by use of a thin beryllium window crystal for counting. The time necessary for the analysis is about 1 h.

A. A. Verbeek,
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AN AUTOMATIC SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF OXYGEN IN STEEL

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M. S. W. Webb and R. J. Webb,
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A HIGH RESOLUTION MASS SPECTROMETRIC MEASUREMENT SYSTEM FOR A VACUUM FUSION APPARATUS

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R. J. Conzemius and H. J. Svec,
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J. M. Ottaway and E. Bishop,
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G. M. Fleck,
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Acid alizarin black SN (AABSN) gives a colour reaction with copper(II) in aqueous solution ($\varepsilon_{650} = 28{,}000$) which provides greater sensitivity than any other method in the visible range of the spectrum except dithizone. The complex is extremely stable, and EDTA can be used to mask most ions. Only Th, Bi, La(III), Fe(III) and Co(II) interfere seriously. The interference of the first 4 can readily be overcome by coprecipitation with aluminium hydroxide.

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M. Hosain and T. S. West,
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E. W. Berg and F. R. Hartlage, Jr.,
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The chelates of various rare earths with acetylacetone, benzoylacetone, dibenzoylmethane, 2-thenoyltrifluoroacetone and dithenoylmethane were prepared and some of their physical properties noted. The ultraviolet absorption spectra in various non-aqueous solvents were measured. Absorption measurements in the visible region showed alterations in absorption intensities and resolution in some of the principal bands, depending on the solvent. The infrared spectra were measured and compared with literature data.

D. Purushotham, V. Ramachandra Rao and (the late) Bh. S. V. Raghava Rao,
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The level of the graph can be arranged to be proportional either to the conductivity or to the concentration of dilute solutions of strontium hydroxide.

I. Holm-Jensen,
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S. Arribas, R. Rincón, R. Moro and M. L. Alvarez,
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R. BELCHER, Y. A. GAWARGIOUS AND A. M. G. MACDONALD,
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(Short Communication)

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(Short Communication)

L. JANKOVICS,
Anal. Chim. Acta, 33 (1965) 225–227

THE EXTRACTION OF ELEMENTS WITH CYCLIC SOLVENTS AND ITS APPLICATION TO GEOCHEMICAL ANALYSIS

C. R. BOSWELL AND R. R. BROOKS

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(Received October 30th, 1964)

Although solvent extraction has long been recognised as a powerful tool in analytical chemistry, its applications in geochemical analysis have been relatively few[1–7]. The crustal abundances of most trace elements are below spectrographic detection limits. The major elements of the earths crust, O, Si, Al, Fe, Ca, Mg, K, Na, and Ti (apart from Fe) do not form chloro-complexes. It should therefore be possible to enrich trace elements in rocks by extraction of their chloro-complexes into organic solvents with subsequent spectrochemical analysis.

Previous workers have shown that the chloro-complexes of many elements are extracted into oxygenated solvents such as diethyl ether and methyl isobutyl ketone[8–14]. Because of reduced steric hindrance, cyclic solvents are better extractants than the corresponding aliphatic compounds[15]. Accordingly, cyclohexanone should prove a more efficient solvent than non-cyclic hexones such as methyl isobutyl ketone.

A method is reported here for the extraction of a range of elements into an organic solvent prior to spectrochemical analysis. The extraction of the elements Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi, from aqueous hydrochloric acid solutions into cyclohexanone has been studied at different acid concentrations. Also, for comparison of relative extracting power, an investigation has been made into the distribution of the same elements between hydrochloric acid and the two solvents cyclohexanol and cyclohexane.

EXPERIMENTAL

Solutions of the elements in the appropriate strength hydrochloric acid were shaken for approximately 30 min with an equal volume of the organic solvent which had been pre-equilibrated with the corresponding strength hydrochloric acid. The solutions were allowed to settle, were separated into two phases, centrifuged and filtered through dry filter paper to ensure complete separation of the phases. Equal volumes of the two phases were mixed with 1 ml of an internal standard solution and 40 mg of Johnson Matthey "Specpure" carbon powder, taken to dryness and arced on a Hilger E742 large automatic spectrograph with quartz optics. The spectrographic operating conditions are given in Table I. Under these conditions, cathode excitation is known to give higher reproducibility[16].

The ratio of the intensity of the analysis line of the element to that of the

TABLE I

SPECTROGRAPHIC OPERATING CONDITIONS

Slit length	12 mm
Slit width	0.15 mm
Wavelength range	2500–3400 Å
Photographic plates	Ilford N-30
Current	7 A D.C.
Excitation	Cathode
Exposure	To completion
Electrodes	Johnson Matthey 4B graphite, 1/16″ internal diameter by 4 mm deep
Photographic processing	4 min at 20° in Kodak D19b developer
Densitometry	Hilger microphotometer with Galvoscale calibrated in B-values[18]
Optical system	Convex quartz lens placed at that slit to give even illumination at this point and to provide an image of the arc at the collimator
Arc gap	4 mm

internal standard was obtained for both the aqueous and organic phases and the percent extraction calculated from the equation:

$$\text{Percent extraction} = \frac{100\,D}{D+r} \tag{1}$$

where

$$D = \frac{(I_x/I_i)_o}{(I_x/I_i)_a}$$

and I_x and I_i are the intensities of the spectral lines of the element and the internal standard respectively, the subscripts o and a refer to the organic and aqueous phases, and r is the ratio of the volumes of the aqueous to the organic phases at equilibrium[17].

TABLE II

INTERNAL STANDARDS, RELATIVE DEVIATIONS AND CONCENTRATIONS

(Lines used were: As 2860, Bi 3067, Cd 3261, Cu 3274, Ga 2943, Hg 2536, In 3256, Pb 2833, Sb 3267, Tl 3229, Zn 3345)

Element	*Concentration*[a] *(g/l)*	*Internal standard*	*Relative deviation*
Zn	1.6	As	10.4
Cd	0.2	Cu	5.9
Hg	4	As	14.7
Ga	0.03	Pb	3.9
In	0.03	Tl	7.4
Tl	1	In	3.6
Sn	0.1	Sb	3.5
Pb	0.1	Ga	4.1
As	1	Sb	6.2
Sb	1	Sn	2.5
Bi	0.03	Pb	5.5

[a] This concentration is the approximate concentration of the element in the aqueous phase before extraction.

The internal standards chosen were those having the lowest relative deviations under the conditions used and are given, together with the relative deviations, in Table II. Lead occurred as an impurity in the internal standard solution and it was necessary to correct for this before substitution in eqn. (1). The concentrations of the elements were adjusted to give intensities in the range 10–200 intensity units[18]. The approximate concentrations of the elements in the aqueous phase before extraction are given in Table II.

All extractions were carried out at 25°. All determinations were done in duplicate and in some cases up to 6 determinations were made.

RESULTS AND DISCUSSION

The percent extraction of the elements as a function of hydrochloric acid concentration for the solvents cyclohexanone and cyclohexanol is shown in Fig. 1. In almost every case there is increased extraction with higher acid concentration and, with the exception of arsenic and tin, all elements have higher percent extrac-

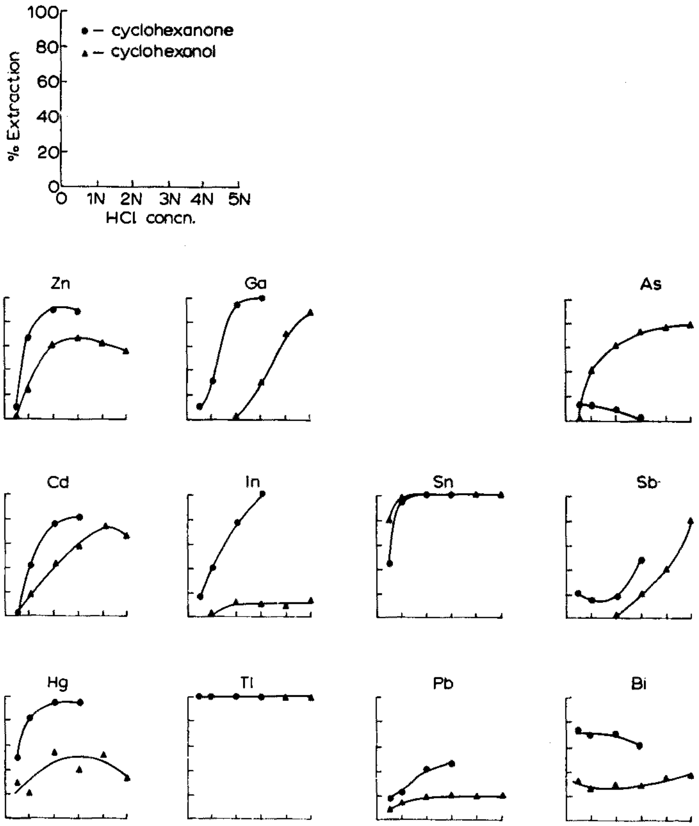

Fig. 1. The extraction of elements into cyclohexanone and cyclohexanol as a function of hydrochloric acid concentration.

tions in cyclohexanone than in cyclohexanol. The results for cyclohexane are not given as they proved to be irreproducible. Three elements were extracted by this solvent: gallium (approximately 5% extraction at all hydrochloric acid concentrations), antimony (very slight extraction) and bismuth (approximately 20% extraction below 3 *N* hydrochloric acid).

Germanium was not determined because of the volatility of its chloride[19].

When cyclohexanone is mixed with a solution approximately 4 *N* in hydrochloric acid a single homogeneous phase is formed. For this reason extraction data for cyclohexanone at acid concentrations greater than 3 *N* were not obtained. For the same reason no results were available for cyclohexanol above 5 *N* hydrochloric acid.

HONSHINO[20] has measured the partition coefficients for zirconium and hafnium with 80 solvents and has found that the values decrease in the sequence: alicyclic ketones, aliphatic ketones, esters, alcohols, ethers.

The results reported here show that in general the extraction into the ketone is greater than into the alcohol (with exceptions in the cases of tin and arsenic).

It is interesting to compare the results reported here with those of KRAUS AND NELSON[21], who obtained the values of the distribution coefficients of the chloro-complexes of a large number of elements between hydrochloric acid and an anion-exchange resin. The trends observed in the solvent-extraction systems parallel closely those in the anion-absorption systems. In many cases an empirical relationship can be shown between the distribution coefficients for anion exchange and solvent extraction (Fig. 2). This relationship is clearly only approximate and needs further investigation. ISHIMORI[22] has noted a similar effect in the extraction of a large number of elements from hydrochloric acid into tributyl phosphate.

It is clear that when these solvents are to be used for the selective extraction

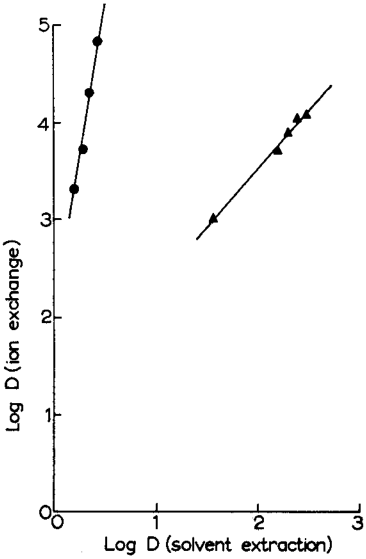

Fig. 2. The relationship between the distribution coefficients for ion exchange and for solvent extraction. ● Bi extracted into cyclohexanone; ▲ Sn extracted into cyclohexanol.

of a particular element, cyclohexanol is more satisfactory than cyclohexanone. For example, indium and thallium in a 0.5 *N* solution of hydrochloric acid can be quantitatively separated with cyclohexanol but not with cyclohexanone. Similarly, tin and lead can be separated more efficiently by cyclohexanol than by cyclohexanone at low acid concentrations.

When an efficient but not selective extracting medium is required, then cyclohexanone with an aqueous phase containing a high concentration of hydrochloric acid is preferable. HALMEKOSKI AND SUNDHOLM[23] have found that ethyl methyl ketone/hydrochloric acid is a better solvent for paper chromatography of cations than cyclohexanone/hydrochloric acid, presumably because the former (a weaker extractant than cyclohexanone) enables the cations to be better separated.

Since cyclohexanone is a good but non-selective extracting medium, it can be used, in conjunction with spectrographic analysis, in trace element determinations in materials of geochemical interest. Preliminary investigations on a granite-gneiss from the Charleston area, New Zealand and a sample of water from Lake Bonney, Antarctica have shown the presence of a large number of trace elements. The elements which have been identified spectrographically in cyclohexanone extracts of solutions of these two materials are listed in Table III.

TABLE III

ELEMENTS DETECTED IN CYCLOHEXANONE EXTRACTS OF A SOLUTION OF A GRANITE-GNEISS AND LAKE BONNEY WATER

Material	*Elements present*							
	Zn	*Cd*	*Ga*	*Tl*	*Sn*	*Pb*	*Sb*	*Bi*
Granite-gneiss	+		+	+	+	+		
Lake Bonney water		+	+	+	+	+	+	+

The authors are indebted to the New Zealand University Research Committee and the Nuffield Foundation for grants towards the establishment of a spectrographic laboratory at Massey University. They are also grateful to the New Zealand Geological Survey, D.S.I.R., for the sample of granite-gneiss and Professor A. T. WILSON, Victoria University of Wellington, New Zealand for the sample of Lake Bonney water.

SUMMARY

The extraction of the elements Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb and Bi into the solvents cyclohexanone, cyclohexanol, and cyclohexane from hydrochloric acid solutions, has been studied. Cyclohexanone is a more efficient but less selective extracting agent than cyclohexanol while cyclohexane has little extracting power. Solvent extraction of hydrochloric acid solutions of materials of geochemical interest into cyclohexanone has been used to enrich trace elements prior to spectrochemical analysis.

RÉSUMÉ

Les auteurs ont examiné l'extraction du zinc, du cadmium, du mercure, du gallium, de l'indium, du thallium, de l'étain, du plomb, de l'arsenic, de l'antimoine et du bismuth dans les solvants: cyclohexanone, cyclohexanol et cyclohexane. La cyclohexanone est un réactif d'extraction plus efficace, mais moins sélectif que le cyclohexanol; tandis que le pouvoir d'extraction du cyclohexane est faible. L'extraction au moyen de cyclohexanone est utilisée pour enrichir des éléments, à l'état de traces, avant leur analyse spectrochimique.

ZUSAMMENFASSUNG

Es wurde die Extraktion der Elemente Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb und Bi mit Cyklohexanon, Cyklohexanol und Cyklohexan aus salzsauren Lösungen untersucht. Cyklohexanon ist am wirksamsten, aber ein weniger selektives Extraktionsmittel als Cyklohexanol, während Cyklohexan nur wenig extrahiert. Die Extraktion aus salzsauren Lösungen mit Cyklohexanon wurde zur Anreicherung von Spurenelementen für die spektrochemische Analyse verwendet.

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NEUTRON ACTIVATION ANALYSIS OF COPPER IN BISMUTH BY γ, γ-COINCIDENCE MEASUREMENT

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Copper has already been determined by activation analysis in numerous materials, as appears from the survey of BOCK-WERTHMANN AND SCHULZE[1,2]. Only KAMEMOTO AND YAMAGISHI[3] and YAKOVLEV *et al.*[4] have determined copper in a bismuth matrix but these workers used a chemical separation. PETIT AND ENGELMANN[5] pointed out that coincidence γ-spectrometry of the annihilation radiation of the β^+ of ^{64}Cu offers the advantages of high specificity and sensitivity for the determination of this element in tantalum. These authors used an annihilation photon as gate signal for the coincidence circuit of a multichannel analyzer, thus reducing other interfering γ-emitters. This technique is however not sufficiently selective for the analysis of copper contents below the p.p.m. range in high-purity bismuth, as

TABLE I

NUCLEAR DATA[8–11]

Target nuclide	*Abundance (%)*	$\sigma_{act.}$	*Isotope produced*	*Half-life*	*Radiation and energy (MeV)*
^{209}Bi	100	0.019	^{210m}Bi	5.0 d	β^- 1.17
^{63}Cu	69.1	3.9	^{64}Cu	12.8 h	β^+ 0.66 (19%) β^- 0.57 γ 1.34
^{64}Zn	49.9	0.5	^{65}Zn	245 d	β^+ 0.325 (1.5%) γ 1.11
^{68}Zn	18.6	0.10	^{69m}Zn	13.8 h	β^- 0.91 γ 0.44
^{75}As	100	5.4	^{76}As	26.4 h	β^- 0.35–2.97 γ 0.56–2.08
^{109}Ag	48.65	2.8	^{110m}Ag	253 d	β^- 0.087; 0.53 γ 0.66–1.51
^{106}Cd	1.22	1.0	^{107}Cd	6.7 h	β^+ 0.32 (0.3%) γ 0.51
^{114}Cd	28.86	0.14 1.1	^{115m}Cd ^{115}Cd	43 d 53 h	β^- 0.19–1.61 γ 0.49–1.30
^{116}Cd	7.58	1.5	^{117}Cd	2.9 h	β^- 1.0 γ 0.27–2.0
^{121}Sb	57.25	6.8	^{122}Sb	2.8 d	β^- 0.73–1.99 γ 0.57–1.26
^{123}Sb	43.75	2.5	^{124}Sb	60.9 d	β^- 0.22–2.31 γ 0.60–2.09
^{197}Au	100	96	^{198}Au	2.7 d	β^- 0.29–1.37 γ 0.412–1.09

random coincidences from the intense bremsstrahlung are still very high. Energy selection with 2 pulse-height analyzers associated with fast coincidence spectrometry further improves the selectivity, as has already been shown by LJUNGGREN[6,7], and allows a very sensitive, non-destructive analysis of copper in high-purity bismuth in the presence of other impurities, such as lead, cadmium, zinc, silver, arsenic, gold, antimony, etc.

Nuclear data

From Table I, which summarizes the most important data, it appears that bismuth is a very favourable matrix for the non-destructive γ-spectrometric determination of trace elements.

Measuring techniques and interferences

Although no γ-rays are emitted from the bismuth matrix or daughter ^{210}Po (Fig. 1a), the energetic β^- of ^{210}Bi gives rise to an important bremsstrahlung as shown in Fig. 2, curve a. From this spectrum it appears that the annihilation radiation at 0.511 MeV of ^{64}Cu is not even detectable at the 0.2 p.p.m. level, although it makes up 19% of the mode of decay (Fig. 1b). The use of one single-channel analyzer which provides the gating signal of the coincidence unit of the 400-channel analyzer, considerably reduces the bremsstrahlung as shown in Fig. 2, curve b (copper content: 0.2 p.p.m.).

If however two single channels are used, with windows corresponding to the energy of the annihilation photons at 0.511 MeV, coupled to a coincidence unit with

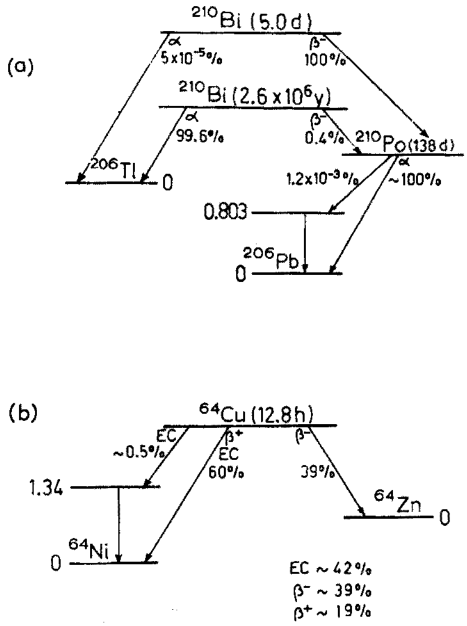

Fig. 1. (a) Decay scheme of ^{210}Bi; (b) decay scheme of ^{64}Cu.

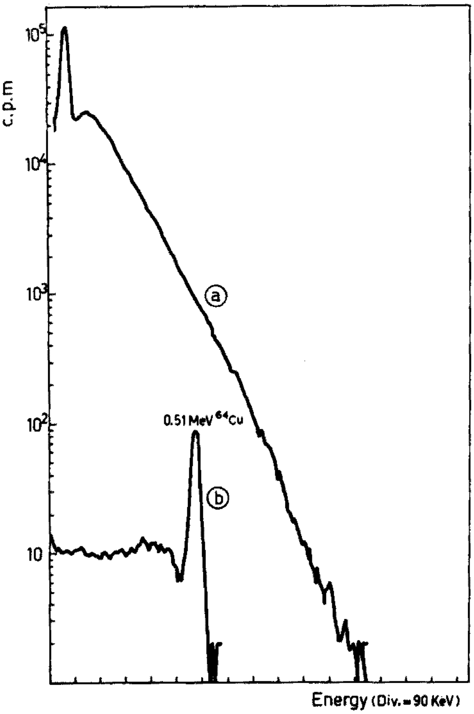

Fig. 2. γ-Ray spectrum of B-2 sample (1 g; 0.226 p.p.m. Cu). (a) Multichannel; (b) single–multichannel coincidence.

a resolving time of 0.1 μsec, random coincidences due to the bremsstrahlung disappear completely as appears from Table II. Even with a relatively large gating window, no detectable activity could be measured from a 1-g high-purity bismuth

TABLE II

SELECTIVE MEASUREMENT OF ^{64}Cu

Window (%)		*Interfering nuclides and activities (counts/min) per μg*						*$^{64}Cu(R_{Cu})$ (counts/min)*	*Ri/R_{Cu}*
Channel A	*Channel B*	*^{198}Au*	*^{110m}Ag*	*^{76}As*	*^{122}Sb*	*^{210}Bi*	*Total act. (Ri)*		
1.70	2.78	0.10	0.00	1.66	0.07	0.00	1.83	254	$7.2 \cdot 10^{-3}$
1.70	5.55	0.66	0.00	1.67	0.07	0.00	2.40	410	$5.9 \cdot 10^{-3}$
1.70	8.35	1.52	0.03	1.67	0.07	0.00	3.29	630	$5.2 \cdot 10^{-3}$
1.70	11.10	1.56	0.07	1.95	0.20	0.00	3.78	796	$4.8 \cdot 10^{-3}$
1.70	13.90	1.96	0.07	1.80	0.13	0.00	3.96	890	$4.5 \cdot 10^{-3}$
1.70	16.65	2.50	0.09	1.66	0.20	0.00	4.45	916	$4.9 \cdot 10^{-3}$
1.70	19.45	3.20	0.14	0.98	0.21	0.00	4.53	1052	$4.3 \cdot 10^{-3}$
1.70	22.20	4.60	0.14	1.70	0.23	0.00	6.67	1140	$5.8 \cdot 10^{-3}$
1.70	25.20	5.50	0.30	1.67	0.33	0.00	7.80	1348	$5.8 \cdot 10^{-3}$
1.70	27.40	6.24	0.50	1.30	0.06	0.00	8.10	1504	$5.3 \cdot 10^{-3}$

sample, irradiated for 12 h at a flux of $8 \cdot 10^{11}$ n/cm²/sec and left to decay during 5 days so as to ensure the complete decay of ^{64}Cu.

The use of a coincidence system decreases the detection efficiency of ^{64}Cu from 19,000 to 410 counts/min/μg, all other variables being equal. This fact, provided that sufficiently long counting periods are possible to ensure adequate counting statistics, is not important in activation analysis, the sensitivity being rather determined by the ratio of the count rate to background. As the background decreases from 150 to 0.02 counts/min, and as a count rate equal to the background can be considered as the lowest detection limit, the sensitivity of the technique is in fact increased from 8 to 0.05 p.p.b. for the irradiating time, neutron flux and sample size mentioned above.

Unavoidable interferences will consequently be mainly due to other β^+ emitting impurities, ^{65}Zn and ^{107}Cd, these elements being also present in high-purity bismuth. Theory and experiment show that a ratio of zinc or cadmium to copper of 10^3 causes an interference of less than 3%. For the bismuth samples under consideration, cadmium and zinc were present in concentrations of the same order of magnitude as copper and corrections were not required.

The influence of other γ-emitting impurities was also investigated, namely ^{198}Au, ^{110m}Ag, ^{76}As and ^{122}Sb. From Table II it is apparent that these elements, irradiated and left to decay in the conditions stated above, do not interfere if their content is of the same order of magnitude as copper.

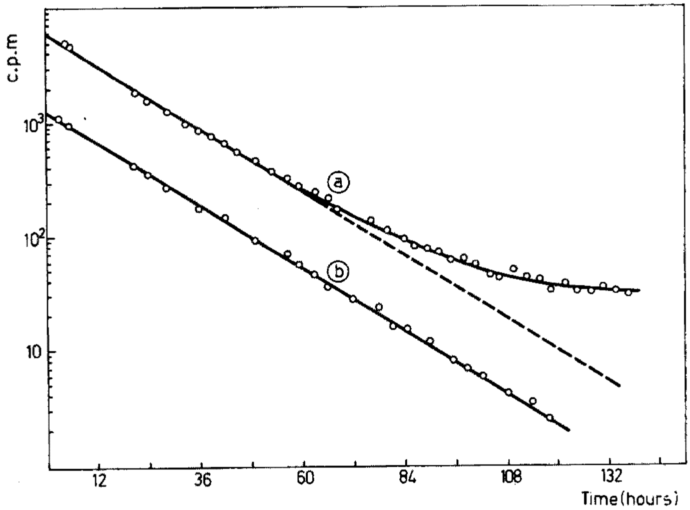

Fig. 3. Decay curve of ^{64}Cu in bismuth. (a) Single–multichannel coincidence; (b) dual single-channel coincidence.

The increase in specificity of the dual single-channel γ, γ-coincidence technique *vs.* the single channel–multichannel system is also apparent from Fig. 3, where a decay curve of ^{64}Cu in the bismuth matrix with the two measuring techniques is given.

Accuracy

As the copper content of a high-purity bismuth rod varied between large limits along the length of the rod, the accuracy of the coincidence technique was tested by spectrophotometry and by destructive activation analysis on reagent-grade granular bismuth. For the spectrophotometric determination, cuproine was used as a specific reagent in the method described by HOSTE *et al.*[12,13]. For the activation analysis after chemical separation, the copper was also separated by isoamyl alcohol extraction of the cuproine–copper complex, followed by gross γ-counting. The results are given in Table III and show that agreement is satisfactory.

TABLE III

DETERMINATION OF COPPER IN BISMUTH (REAGENT GRADE)

Sample no.	*Spectrophotometry*	*Destructive act. anal.*	*Coincidence technique*
1	38.3	37.3	38.7
2	38.1	36.6	37.4
3	38.7	35.1	38.9
4	37.3	39.4	37.5
5	37.0	38.4	37.3
Mean value	37.9 ± 0.7 p.p.m.	37.4 ± 1.7 p.p.m.	38.0 ± 0.8 p.p.m.
S.D.	1.9%	4.5%	2.1%

TABLE IV

ACTIVATION ANALYSIS OF COPPER IN BISMUTH

Sample	*Non-destructive method (p.p.m.)*	*Destructive method (p.p.m.)*
B-2[a]	0.940	1.020
	0.983	1.010
	0.665	0.681
	0.453	0.497
	0.398	0.408
B-3	0.181	0.191
	0.045	0.051
	0.019	0.021
B-4	0.096	0.089
	0.071	0.075
	0.027	0.031

[a] First quarter of rod B-2.

The agreement between the coincidence and conventional γ-spectrometry was also tested on high-purity samples (B-2, B-3 and B-4, see below) by first counting the untreated samples by the coincidence technique, and afterwards counting the separated copper fraction by multichannel γ-spectrometry. The results are given in Table IV.

Application

Activation analysis of copper was tested on a high-purity bismuth rod which was cut into slices of approximately 1 g.

EXPERIMENTAL

Apparatus

(1) Two 3″ × 3″ NaI(Tl) crystals and EMI 9531A multiplier phototubes.
(2) White cathode followers.
(3) Nuclear Enterprises Linear Amplifiers NE 5202 (Fairstein type).
(4) Pulse-height analyzers (Fairstein type).
(5) Tracerlab coincidence–anticoincidence unit RLA-6A.
(6) Tracerlab precision High Voltage Supply RL-S-8.
(7) Bell Telephone Mfg Co scaler NUK 197-AI.
(8) Intertechnique 400-channel analyzer SA-40.

Procedure

Pack slices of *ca.* 1 g of bismuth and 5 mg of electrolytic copper in aluminium. Irradiate for 12 h in the BR-1 reactor at a flux of approximately $8 \cdot 10^{11}$ n/cm^2/sec. After a decay period of *ca.* 12 h, treat the samples with dilute nitric acid to remove surface contamination. Wash, dry and mount on counting planchets. Place the

TABLE V

ACTIVATION ANALYSIS OF COPPER IN BISMUTH

Sample	*Measurements at 3-h interval*	*Mean value found (p.p.m.)*	*S.D. (%)*
B-2 (unknown purity)	4	0.423 ± 0.016	3.8
	4	0.240 ± 0.022	9.2
[a]	4	0.208 ± 0.010	4.8
	4	0.153 ± 0.010	6.5
	4	0.130 ± 0.008	6.2
	4	0.128 ± 0.010	7.8
	6	0.135 ± 0.005	3.7
	6	0.071 ± 0.004	5.6
[a]	6	0.070 ± 0.003	4.3
	6	0.066 ± 0.001	1.5
	6	0.039 ± 0.002	5.1
	6	0.039 ± 0.001	2.5
[a]	6	0.033 ± 0.002	6.0
	6	0.031 ± 0.002	6.5
	6	0.029 ± 0.002	7.7
B-3 (99.999%)	5	0.006 ± 0.0004	6.7
	5	0.010 ± 0.0005	5.0
	5	0.019 ± 0.0021	11.0
	5	0.088 ± 0.0031	3.5
	5	0.016 ± 0.0017	10.6
	5	0.047 ± 0.0042	8.9
	5	0.040 ± 0.0022	5.5
B-4 (99.9999%)	4	0.039 ± 0.0036	9.2
	4	0.022 ± 0.0019	8.7
	4	0.072 ± 0.0061	8.5
	4	0.074 ± 0.0069	9.3
	4	0.027 ± 0.0021	7.8
	4	0.031 ± 0.0021	6.8

[a] Resp. quarters of rod B-2.

sample at an equal distance from the detectors (1 cm) and count for 5 min, repeating this every 3 h. Count the background for 10 h.

Dissolve the standards in 6 N nitric acid and make up to 500 ml; take a 100-μl aliquot, transfer to a counting planchet, evaporate to dryness and count in the same geometrical conditions. Compute the copper content from the ratio of the count rates and the weight of copper in the standards.

RESULTS

Three high-purity bismuth samples B-2, B-3 and B-4 were analysed (Table V). From the different analyses of each sample it appears that the distribution of copper in bismuth is quite irregular. For samples B-3 and B-4 it was not possible to determine whether a concentration gradient was present as only chunks were available.

Sample B-2, however, was a rod, *ca.* 15 cm long and 0.8 cm diameter. From this 20 slices were cut and analyzed. Plotting the results according to their respective location, Fig. 4 could be drawn, clearly indicating a concentration gradient in the rod.

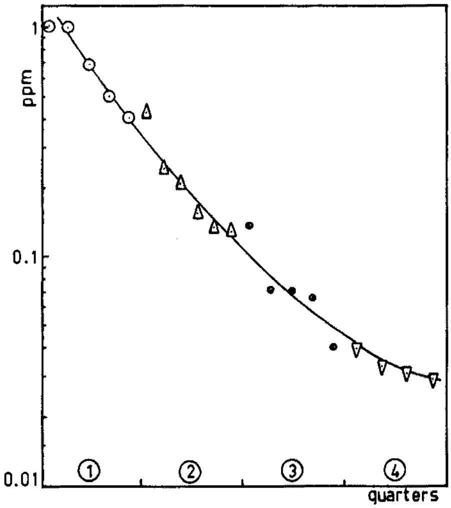

Fig. 4. Distribution of Cu along B-2 rod.

SUMMARY

Copper was determined non-destructively by neutron activation analysis in high-purity bismuth down to concentrations of 30 p.p.b. By using γ, γ-coincidence counting of the annihilation photons of ^{64}Cu, interferences from the bremsstrahlung of the matrix could be completely suppressed, together with the interferences due to the induced γ-activities of other impurities as Zn, Cd, Au, Ag, Sb and As.

The accuracy of the method was tested by spectrophotometry and by destructive activation analysis. The technique was applied to the analysis of a high-purity bismuth rod.

RÉSUMÉ

Une méthode est proposée pour le dosage "non-destructif" du cuivre (jusqu'à 30 p.p.b.), dans du bismuth de haute pureté, par activation au moyen de neutrons. Par mesure de coïncidence γ–γ, les interférences provenant de la matrice peuvent être complètement supprimées, de même que les interférences dues aux activités-γ induites d'autres impuretés, telles que Zn, Cd, Au, Ag, Sb et As. L'exactitude de la méthode a été déterminée par spectrophotométrie et par analyse par activation destructive.

ZUSAMMENFASSUNG

Kupfer wurde in hochreinem Wismut bis hinab zu Konzentrationen von 30 p.p.b. zerstörungsfrei mit der Neutronenaktivierungsanalyse bestimmt. Durch γ–γ-Koinzidenzzählung der Vernichtungsstrahlung des ^{64}Cu werden durch die Bremsstrahlung hervorgerufene Störungen völlig unterdrückt, gleichzeitig mit den Störungen, die durch Aktivitäten anderer Verunreinigungen wie Zn, Cd, Au, Ag, Sb und As hervorgerufen werden.

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THE DETERMINATION OF NIOBIUM IN STEEL BY NEUTRON ACTIVATION

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The many methods applicable to the determination of niobium and tantalum have been reviewed by COCKBILL[1], who also suggested a general method of approach for all samples. For relatively high concentrations of niobium, the recommended method is that described by HUNT AND WELLS[2], both metals being determined via their pyrogallol complexes. Trace concentrations of niobium may be determined using paper-strip chromatography and subsequent spectrophotometric measurements; in this way HUNT, NORTH AND WELLS[3] were able to extend the lower limit of measurement to 0.0004 % niobium pentoxide.

Stable niobium is mono-isotopic and on slow neutron activation forms the 6.6-min niobium-94m. This isomeric state decays by emission of a highly converted γ-ray, and it is the 16.7-keV X-ray emitted as a result of the conversion process which must be measured in any determination of niobium by slow neutron activation. Rapid separations of niobium are thus required, and this, together with the low energy of the X-ray emitted, makes activation analysis for niobium difficult. Recently, however, KIM[4], and KIM AND MEINKE[5] have reported determinations of niobium and tantalum based on slow neutron activation and measurement of the 16.7- and 57.8-keV X-rays from niobium-94m and tantalum-182m respectively. KIM AND MEINKE report values for niobium in the granite G-1 and in a stainless steel sample. Their value for the niobium content of G-1 (32 ± 3 p.p.m.) is about 4 times higher than previously reported values, although, as they remark, some deviation might be due to inhomogeneity of the G-1 sample. The value they report for the steel sample (0.58 ± 0.05%) compares well with the reported value.

The present work was started before the publication of the paper of KIM AND MEINKE. It was felt that slow neutron activation analysis should lead not only to a more rapid but also a more sensitive method for the determination of niobium than is possible by purely chemical means. The estimated ultimate sensitivity of detection for niobium[6] is 0.005 ng/g. It was hoped to test the method on samples of standard steels and then to extend it to provide a method of analysis for niobium in iron meteorites.

EXPERIMENTAL

Because of the low energy of the niobium-94m X-ray, the sample prepared for

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counting must be free from nuclides emitting higher-energy γ-rays if the niobium photopeak is not to be superimposed on a high background resulting from the Compton scattering of such γ-rays, or even lost within it. This requirement, and that of a quick separation, led to the investigation of solvent extraction procedures as the basis of the method for the separation of niobium.

Niobium may be almost quantitatively extracted from solutions containing high concentrations of hydrofluoric acid in the presence of one or more other mineral acids. These methods give good separations of niobium and tantalum from many other elements. FAYE AND INMAN[7] have shown that methyl isobutyl ketone extracts over 90% of tantalum but less than 1% of niobium from solutions 0.5 M in hydrofluoric acid and 1 M in nitric acid, and almost quantitatively extracts both metals in high purity from solutions 7 M in hydrofluoric acid and 5 M in nitric acid. Since mild steels and iron meteorite samples were found to dissolve readily in mixtures of nitric acid and hydrofluoric acid, it was decided to use the hexone–hydrofluoric acid–nitric acid system in preference to the others. KIM AND MEINKE[5] regarded "methylisobutylketone extraction" as giving a seriously contaminated separation, but did not state the acid system used in their extraction.

Because speed of separation was essential, the final precipitation of the extracted niobium by tannic acid was undesirable because of the bulk of the precipitate obtained and because of its slow filtration. Hydrolytic precipitation was favoured since hydrolysis can be achieved from solutions containing oxalo- or tartaro-complexes as well as from niobate solutions. In view of this, and because stripping of niobium from hexone solution should be more readily obtained by complexing solutions, the effect of various solutions of oxalic acid as stripping agents was investigated. It was found that half-saturated aqueous oxalic acid was most effective, one equal-volume extraction stripping over 80% of the niobium present in the organic phase. Hydrated niobium pentoxide can be precipitated from this stripping solution by addition of ammonia solution.

The chemical yield of niobium was determined by an activation analysis of the final samples, prepared for counting, after the originally induced activity had died away. This method was chosen because it is simple and rapid and was shown to give accurate results provided that not more than about 4.5 mg of niobium pentoxide was present. The upper limit is necessary since sample self-absorption is evident with greater quantities. The figure quoted will vary with the diameter of the container used to hold the precipitate, but must be taken into account when considering the weight of carrier which can be used in the determination.

Irradiation

Steel samples, in polytainers, and standard solutions of niobium, sealed in polythene, were irradiated side by side for 10 min in a flux of about $1.2 \cdot 10^{12}$ n/cm²/sec in the Harwell reactor, BEPO. The samples were delivered to and from the reactor by means of a "rabbit" system which delivered the irradiated samples within 2 min after irradiation had ceased.

Reagents

All reagents used were of analytical-reagent grade unless otherwise stated.

Methylisobutylketone. Redistilled commercial grade, (*a*) equilibrated with an aqueous solution 0.5 *M* in hydrofluoric acid and 1 *M* in nitric acid; (*b*) equilibrated with an aqueous solution 7 *M* in hydrofluoric acid and 5 *M* in nitric acid.

Niobium standard solution. "Specpure" niobium metal (400 mg) was dissolved in a minimum of hydrofluoric acid to which had been added a few drops of nitric acid. The solution was diluted to 100 ml with water and stored in polythene.

Chemical separation

Since speed of separation was essential, all solutions, reagents and apparatus had to be ready for immediate use before the irradiation began.

(a) Mild steel samples. Immediately the sample and standard solution returned from the reactor, the steel sample was transferred to a platinum dish containing a solution of a known weight of niobium metal (about 10 mg) and about 5 mg of tantalum metal in 0.3 ml of 40%(w/v) hydrofluoric acid, 1.7 ml of 16 *N* nitric acid and 1 ml of water. After the initial vigorous reaction had subsided, the solution was warmed and a further 7 ml of water were added. The resulting solution was well stirred and then extracted with 10 ml of hexone previously equilibrated with 0.5 *M* hydrofluoric acid and 1 *M* nitric acid. The aqueous layer was separated and 7 ml of 16 *N* nitric acid and 8 ml of 40%(w/v) hydrofluoric acid were added to it. This solution was then extracted with 25 ml of hexone previously equilibrated with 7 *M* hydrofluoric acid and 5 *M* nitric acid. The organic phase was then stripped of niobium by extraction with 25 ml of 4.8%(w/v) oxalic acid solution. The aqueous layer was run into a beaker containing 2 g of boric acid and 2 ml of 0.1 *M* EDTA solution (disodium salt). After stirring, the mixture was made alkaline to phenolphthalein, by addition of 15 *N* ammonia solution, and then heated to just under boiling point for 1 min. The precipitate was centrifuged off and washed once with diluted nitric acid (1 + 1). The polythene centrifuge tube was thoroughly drained and the precipitate slurried with acetone. The precipitate was then filtered through a disc of Whatman accelerator paper, backed by a disc of No. 30 Whatman paper supported by a sintered glass filter stick. The discs of paper were cut so that they were slightly larger in diameter than the filter stick but just fitted into the polytainer used to hold the sample for counting.

The time taken for this procedure was about 11 min.

(b) Stainless steel sample. The carriers for the steel sample were dissolved in 0.2 ml of 40%(w/v) hydrofluoric acid containing a few drops of nitric acid in a small teflon beaker, and 0.5 ml of aqua regia was added to the solution. The irradiated steel sample was dissolved in this mixture and evaporated to dryness using a low-temperature hot plate and infrared lamps. The residue was dissolved, with heating, in a mixture of 1.7 ml of 16 *N* nitric acid, 0.3 ml of 40% hydrofluoric acid and 8 ml of water. The solution was extracted with 10 ml of hexone previously equilibrated with 0.5 *M* hydrofluoric acid and 1 *M* nitric acid. The separation of the niobium was then carried out exactly as in the case of mild steel samples starting at the point where the acidity of the solution was adjusted by addition of 8 ml of hydrofluoric acid and 7 ml of nitric acid.

The time taken for this procedure was about 20 min.

(c) Standards. In the case of analysis of mild steels, the steel samples were separated and counted before work on the irradiated standard solution was begun. In the case of the stainless steel sample, the standard was processed while the acid solution of the steel was evaporating to dryness. 0.25 ml of the irradiated solution was withdrawn and added to a solution of a known weight of niobium metal (about 5 mg)

dissolved in a few drops of 40% hydrofluoric acid and one drop of 16 *N* nitric acid and diluted to about 20 ml. The solution was well stirred and 2 g of boric acid were added. The niobium was then precipitated by addition of ammonia solution and prepared for counting as in the case of the steel samples.

Determination of activity

The precipitates, mounted on paper discs by filtration, were placed in polytainers so cut that the solid sectioned cap when pushed home kept the discs firmly in place on the bottom of the polytainer. The activity of the sample was then determined by placing the polytainer on an aluminium-clad, 1.5 in, sodium iodide crystal coupled to a Laben 512-channel analyser, and counting for periods of 64 live sec. At least 5 counts were made. The printed output of the system was then used to determine the activity represented by the photopeak after correction for background and baseline activity had been made. The activity of the sample at some chosen time was then calculated by taking the average value of the various counts, taken for any sample, referred to this time. The results were also used to plot a decay curve for the sample and to plot out the γ-ray spectrum of the sample.

Determination of yield

Three samples of "Specpure" niobium pentoxide (usually about 0.8, 1.5 and 2.5 mg) were weighed out into specially cut polytainers similar to those used to hold the samples for counting. The powder was evenly spread over the bottom of the polytainer, covered with a disc of Whatman accelerator paper, and the cap was pushed home firmly. These standards, together with the previously counted steel and standard precipitates were then irradiated together for a period of about 20 sec. After cooling for 20 min the samples were counted as previously described except that a thin sheet of cellophane covered the outer casing of the crystal as a protection against accidental contamination. The activity of each sample at some arbitrarily chosen time was then calculated from the average of at least two counts on each sample. The chemical yields for the steel and standard samples were then calculated.

RESULTS AND DISCUSSION

The results obtained are shown in Table I.

Errors

It has already been shown by KEMP AND SMALES[8] that the flux gradients in the "rabbit" system used are not serious provided that the top half of the "rabbit" is used. This was always done during these irradiations. The most likely cause of error in the irradiations performed would be the time taken for the "rabbit" to enter and leave the reactor when the short irradiations for yield determination were being made. For this reason the time of irradiation was far longer than necessary, in order that the time taken to enter and leave the reactor was short compared with the total time of irradiation. Self-shielding effects, which may be present during the irradiation of the steel samples, have already been discussed in general by GILAT AND GURFINKEL[9] and by HØGDAHL[10], and are unlikely to give rise to errors greater than about 1%.

The "Specpure" samples of niobium metal and niobium pentoxide were shown

TABLE I

RESULTS

Sample	*Approx. weight taken (mg)*	*% Nb found*	*Mean*	*Certificate details*
B.C.S. 261	20	0.67, 0.71, 0.69	0.69 ± 0.02[a]	0.71% (Nb + Ta, calculated as Nb). One analyst gives 0.67% Nb, 0.04% Ta
B.C.S. 271	70	0.133, 0.144, 0.136	0.14 ± 0.006	0.11% (Chemical) 0.13% (Spectrographic)
B.C.S. 275	200	0.044, 0.042, 0.043	0.043 ± 0.001	0.035% (Chemical) 0.030% (Spectrographic)
B.C.S. 277	200	0.022, 0.023, 0.022	0.022 ± 0.001	0.021% (Chemical) 0.020% (Spectrographic)

[a] Standard deviation.

to exhibit straight-line decay "curves" of half-life close to 6.60 min over periods of up to 5 half-lives. Although in the case of the samples and standards analysed, observation could not be made over such extended periods, the decay curves showed no evidence of mixed activities as may be seen from Fig. 1. This conclusion is strengthened by the fact that no other peaks could be observed in the low-energy region of the γ-spectrum even when the niobium photopeak had died away. This is illustrated in Fig. 2. It was found, however, that in the presence of higher concentrations of cobalt such as are present in iron meteorites (0.6%) when irradiation was in fluxes of the order $3 \cdot 10^{14}$ n/cm²/sec, some cobalt activity (^{60m}Co has a half-life of 10.5 min, and shows photopeaks in the region of 60 keV and 25 keV) was observed. The cobalt photopeak of lowest energy interfered with the measurement of the niobium activity, but the use of cobalt carrier both at the initial solution stage and again at the precipitation stage was found to eliminate this effect.

Possible errors which may arise due to nuclear reactions other than the (n,γ) reaction must also be considered. Niobium-94m may also be produced by the (n,p)

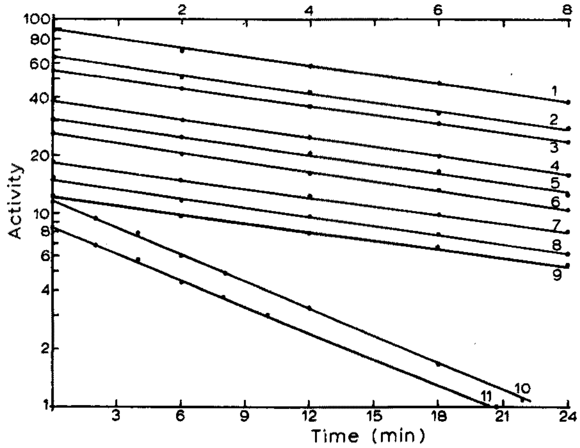

Fig. 1. Decay curves from niobium determinations. The lower time axis applies only to curves 10 and 11. Curves 10, 11—B.C.S. 261; curves 1, 5, 6—B.C.S. 271; curves 2, 3, 9—B.C.S. 275; curves 4, 7—B.C.S. 277; curve 8—standard niobium sample.

and (n,pn) reactions on molybdenum. Neither reaction is likely to lead to any error unless the niobium is present in a molybdenum matrix. Nevertheless, 40 mg of molybdenum trioxide were irradiated for 10 min, mixed with niobium carrier and the niobium then separated. The γ-spectrum of the sample showed no evidence of the presence of a niobium-94m photopeak clearly distinguishable above the background.

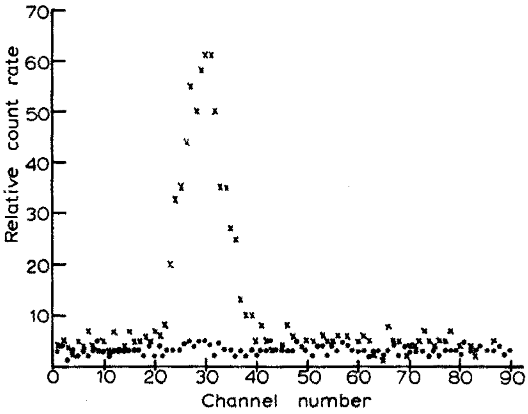

Fig. 2. γ-Spectra showing ^{94m}Nb photopeak. × t = 15 min; ● = 50 min.

Counting errors are probably the most serious errors involved in this determination, for the half-life of the nuclide produced is short and it is not possible to count samples for long periods in order to decrease statistical fluctuations. In addition, the times at which various counts are taken must be accurately known and it is desirable to use a stop watch for this purpose.

Method

The method gives results which compare reasonably well with the values quoted on the certificates issued by the Bureau of Analysed Samples Ltd. The greatest deviation from the published value occurs in the case of B.C.S. 275. No reason can be given for this result being so high. Careful scrutiny of the decay curves and γ-ray spectra from this sample revealed no reason to consider this result less accurate than the others.

On the basis of a 200-mg steel sample, the method should be applicable down to niobium concentrations of the order of 15 p.p.m., *i.e.* 3 μg of niobium, assuming that at least 3 counts of activity above 100 counts/min are to be obtained. This value is disappointingly high. One reason for the high limiting value is the poor chemical yield of the separation process. The average yield for steel samples was around 11%, and for the standards, about 25%. The low value for the yield in the case of the standards, together with the satisfactory recoveries from the solvent extraction steps, indicates that the major loss occurs in the precipitation and filtration stages. The second reason for lack of sensitivity lies in the absorption of the low-energy radiation from niobium-94m by the aluminium casing of the sodium iodide crystal. Calculations and preliminary experiments show that the count rate from a given sample can be increased by a factor of about 10 by using a thin crystal with a thin (0.008 in) beryllium window. The thin crystal has the advantage of being transparent to any high energy γ-radiation which may be present. A further increase in sensitivity could be attained by using the high flux available in reactors such as DIDO, although the use of high fluxes may involve extra stages in the separation procedure.

ACKNOWLEDGEMENTS

The author thanks the South African C.S.I.R. for a bursary which made this work possible, the U.K.A.E.A. for the facilities placed at his disposal while attached to the staff at Harwell, and Mr. A. A. SMALES for interesting and critical discussions.

SUMMARY

A method is described for determination of niobium in steels by neutron activation analysis. It is applicable to samples containing down to 3 μg of niobium; but this sensitivity may be improved by a factor of 10 by use of a thin beryllium window crystal for counting. The time necessary for the analysis is about 1 h.

RÉSUMÉ

On décrit une méthode pour le dosage du niobium dans les aciers par analyse par activation au moyen de neutrons. Elle est applicable à des échantillons renfermant un minimum de 3 μg de niobium. Cette sensibilité peut être encore améliorée de 10 fois, en utilisant une fenêtre de béryllium mince pour le comptage. La durée d'une analyse est d'environ une heure.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Niob im Stahl mittels der Neutronenaktivierungsanalyse beschrieben, mit der sich bis hinab zu 3 μg Niob bestimmen lassen. Diese Empfindlichkeit kann bei Anwendung eines Zählkristalls mit dünnem Berylliumfenster noch um den Faktor 10 verbessert werden. Für die Analyse wird etwa 1 Std. benötigt.

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AN AUTOMATIC SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF OXYGEN IN STEEL

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In recent years there have been considerable advances in analytical methods for the determination of gaseous elements in metals. In this connection we have been interested in the development of a device for the determination of oxygen in small samples of steel which would be relatively inexpensive and at the same time simple enough to permit some degree of automation so that the process could be speeded up.

In the past we have used high-temperature hollow cathodes to determine trace elements in refractory oxides and the resulting spectra have shown the presence of the oxygen multiplet at 7772/5 Å. This suggested a possible means of determining oxygen in metals.

Some years ago, ROSEN AND OTTLET[1,2] used this type of spectrographic source for the determination of oxygen by extracting carbon monoxide into argon atmospheres and measuring the intensity of the carbon monoxide band heads in emission and absorption. For our particular purpose this technique suffered from a number of disadvantages. Firstly it was insufficiently sensitive to permit the determination of oxygen in small samples weighing 20–200 mg; secondly the argon caused sputtering of the metal atoms into the discharge and this made the use of an internal standard essential; and lastly it has been said that the method does not hold its calibration very well and restandardisation is necessary with each batch of samples[3].

In our experience the use of a high-temperature hollow-cathode discharge operating in helium obviated most of the difficulties.

EXPERIMENTAL

In principle the method consists of using a graphite hollow cathode operating at a temperature of 1850° to melt the sample and excite the atomic spectrum of oxygen.

The general layout of the apparatus is shown in Fig. 1.

The graphite hollow cathode is contained in a water-cooled stainless steel chamber filled with clean helium at a pressure of 8 ± 0.5 mm. The helium scavenging train is fitted with electromagnetic valves and is conventional in that the gas is circulated by means of a mercury diffusion pump through a glass and metal system and scavenged by means of activated charcoal immersed in liquid nitrogen.

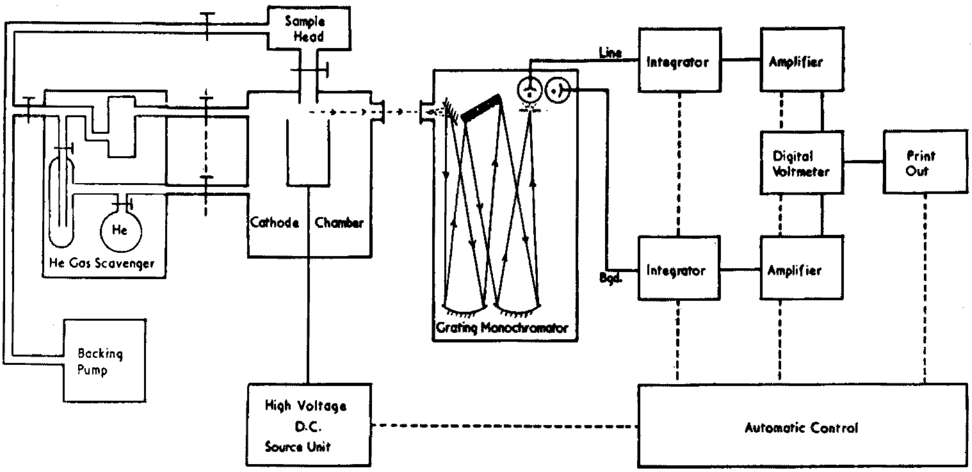

Fig. 1. Schematic layout of the apparatus.

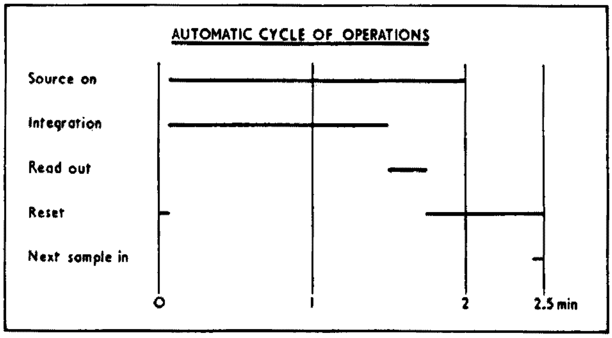

Fig. 2. Cycle of operations.

The light emitted by the source is examined in a direction at right-angles to the cathode axis, in order to minimise the high background associated with the interior of the hot cavity. The radiation is dispersed by means of a small monochromator designed on a Czerny–Turner mounting and having a reciprocal linear dispersion of 20 Å/mm and a focal length of 27 cm. Exit slits and mirrors are so arranged that an E.M.I. red-sensitive photomultiplier records the intensity of the oxygen 7772/5 Å multiplet, whilst the adjacent background radiation is reflected by means of a mirror on to another photomultiplier. The electronic circuits consist of stabilised power supplies and integrators of conventional design, the output from the photomultipliers being accumulated in 0.25 μF condensers during the fixed integration period of 90 sec, the charge on the respective condensers being proportional to the integrated light flux. The difference in output of the two electrometer circuits is recorded on a digital voltmeter linked to an automatic print-out.

The whole cycle of operations involving the operation of the source, integration of signals and print-out is accomplished automatically on a 2.5-min cycle by means of a sequence timer. The co-ordination of the various parts of this repetitive cycle is demonstrated in Fig. 2. The sample is dropped into the cathode and the source and integrators are switched on automatically after 3 sec. An integration of 90 sec was found to be the optimum to record the oxygen signal in a dynamic system. After this period the integration stops and the difference in integrated signals is read out. After 2 min the source is switched off and the next sample is fed into the cathode 30 sec later.

Hollow-cathode chamber

Most of the equipment is conventional except for the hollow-cathode chamber and a diagrammatic section of this is shown in Fig. 3. The cathode is machined from

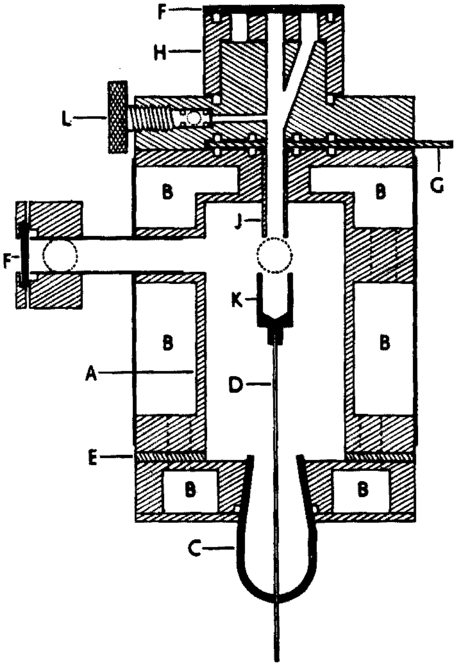

Fig. 3. Cathode chamber. (A) stainless steel cathode chamber; (B) water jacket; (C) standard B24 pyrex glass joint; (D) 2 mm tungsten rod; (E) sheet rubber gasket; (F) quartz windows; (G) shutter; (H) turret sample head; (J) anode (at earth potential); (K) cathode; (L) valve.

"pile-grade" graphite and mounted on a tungsten rod, the whole assembly being sealed into the container by means of a greased B24 pyrex joint. The anode consists of 3/8-in. i.d. removable steel sleeve situated 0.5 in. above the cathode. The chamber is surmounted by a turret-head consisting of a cylindrical block drilled with 9 holes, each hole containing a sample which may be released into the cathode by rotating the head until the appropriate sample cavity is aligned with the hole drilled in the head-plate of the cathode chamber. The sample head may be separated from the hollow-cathode chamber by means of a steel shutter-plate. This enables the turret head to be let up to atmospheric pressure, reloaded with samples by removing the quartz plate and then evacuated without affecting the conditions in the remainder of the apparatus.

Outgassing of the cathode

The graphite cathode is outgassed by running the discharge and scavenging the gas stream. It has been found in practice that this takes 30–40 min for completion of outgassing. Once this has been done, a single cathode can be used for 27 determinations without further treatment.

Experiments with cathodes constructed from pyrolytic graphite showed that the outgassing time is shorter with this material but the discharge tends to be unstable owing to the fact that the molten steel does not completely wet the graphite. Where a high sample turn-over is required it is convenient to have an auxiliary hollow-cathode chamber and gas-scavenger to outgas one cathode whilst another is being used for determinations.

Operating conditions

For the determination of oxygen in steel no bath is necessary and samples weighing from 20–200 mg are dropped directly into the hollow cathode. Conditions are so arranged that the sample melts and gas is liberated without iron atoms entering the discharge, making internal standardisation unnecessary. For steel these conditions are obtained with a pressure of 8 mm of helium, and the current is maintained at 0.85 A, the potential difference being about 500 V.

Generally an operating cycle of 2.5 min is adequate to allow complete removal of oxygen from the previous sample but when amounts of oxygen in excess of 20 μg have been determined it is advisable to run a blank determination before analysing the next sample.

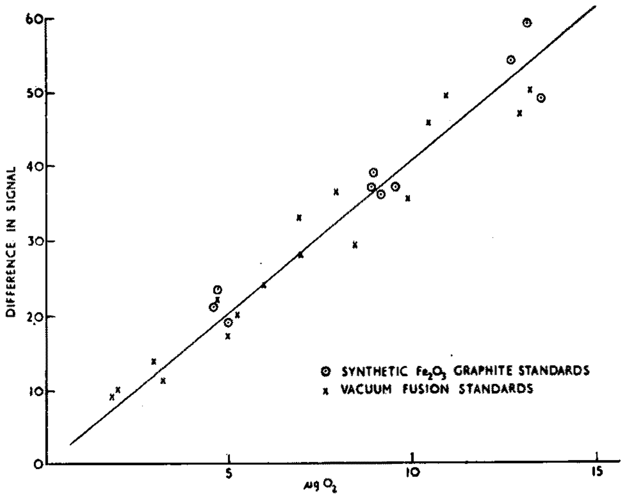

Fig. 4. Calibration curves comparing standardised samples and synthetic standards.

Calibration

Originally the apparatus was standardised by using samples of steel, the oxygen content of which had been established by the vacuum fusion method. More recently pellets of flake graphite weighing 10 mg and containing known amounts of oxygen in the form of ferric oxide were used and identical calibration graphs were obtained (Fig. 4).

The instrument holds its calibration almost indefinitely and in practice it was found sufficient to multiply the line and background difference by a factor, provided that a sample of known oxygen content was determined from time to time for quality control purposes. The main limiting factor on the stability of performance of the instrument appears to be the cleanliness of the glass window situated between the hollow-cathode chamber and the monochromator—this window needs cleaning about once a month.

RESULTS AND DISCUSSION

The standard deviation of the background in the 7772 Å region was equivalent to 0.3 μg so that the 3 σ limit of sensitivity for oxygen is better than 1 μg.

Replicate analyses of the sample used for quality control purposes showed a coefficient of variation of 12% at the 200 p.p.m. level for a single determination. In view of the small sample weight used it is considered that this figure is satisfactory. For cold-drawn steels in which the oxygen content was more homogeneously distributed, coefficients of variation of 6% were obtained.

To check the accuracy of the technique the oxygen contents of a number of steels of different composition were determined by the hollow-cathode method, by neutron-activation analysis and by vacuum fusion methods. The results quoted in Table I are means of duplicate or triplicate determinations except for those obtained by the hollow-cathode method using vacuum fusion standards, which were the means of 6 determinations. This replication was undertaken to compensate, in part, for the heterogeneity introduced by the use of small samples. Good agreement is evident

TABLE I

DETERMINATION OF OXYGEN IN STEEL—COMPARATIVE ANALYSES

Sample	*p.p.m.Oxygen in steel*			
	Vacuum fusion	*Neutron-activation analysis*	*Hollow cathode*	
			Vacuum fusion standards	*Fe_2O_3 synthetic standards*
Low alloy steel 1	145	—	160	150
Low alloy steel 2	100	—	90	—
Low alloy steel 3	35	—	40	45
Mild steel	65	90	95	90
Stainless 18/12/1	80	77	80	105
Stainless 18/8/1	35	18	15	25
Stainless 25/20	180	135	180	150
Low manganese steel	175	—	160	165
Manganese steel	200	210	200	220
Silicon-killed steel	180	155	150	—

between the results obtained by the neutron-activation and hollow-cathode methods except for sample "stainless 25/20" where there is better agreement with the vacuum fusion results. Statistical analysis of all the results indicated that there is no significant difference in the results obtained by any of the methods.

The potentialities of this device have not been fully explored and it is considered that the simultaneous determination of oxygen, hydrogen and nitrogen in steel and a variety of other materials should be feasible.

Grateful acknowledgement is made to the following for assistance with this project: The British Iron & Steel Research Association for supplying some of the samples of steel; Mr. H. I. SHALGOSKY who arranged for analysis by the vacuum fusion method; Dr. C. A. BAKER for neutron-activation analysis; Mr. YOUENS for much of the construction work, and The Chemical Inspectorate, Ministry of Defence, for construction of the hollow-cathode chamber and for glass-blowing services.

SUMMARY

A device for the determination of oxygen in steel (20–200 mg samples) is described. A high temperature hollow-cathode discharge is used to melt the sample and excite the atomic spectrum of oxygen. A compact grating monochromator fitted with two red-sensitive photomultipliers is used to record the difference in integrated intensity between the oxygen multiplet at 7772/5 Å and the adjacent background during a fixed integration period, the corresponding voltage difference being presented on a digital voltmeter linked to an automatic print-out. The automatic cycle of operations takes 2.5 min per sample. The sensitivity of the technique is 1 μg O. The coefficient of variation per determination varies from 6 to 15% depending upon the homogeneity of the sample.

RÉSUMÉ

Un dispositif est décrit pour le dosage de l'oxygène dans l'acier (échantillons de 20 à 200 mg). Il comprend: décharge cathodique à haute température pour fondre l'échantillon et exciter le spectre atomique de l'oxygène, et monochromateur à réseau compact, muni de deux photomultiplicateurs sensibles au rouge. Le cycle automatique des opérations demande 2.5 min par échantillon. Sensibilité: 1 μg d'oxygène. Le coefficient de variation par détermination varie de 6 à 15%, suivant l'homogénéité de l'échantillon.

ZUSAMMENFASSUNG

Es wird eine automatische spektrographische Methode zur Bestimmung von Sauerstoff in Stahl (20–200 mg Proben) beschrieben. Zum Schmelzen der Probe und zur Anregung des Atomspektrums wird eine Hochtemperatur-Hohlkathodenentladung benutzt. Mit Hilfe eines Gittermonochromators und zwei rotempfindlichen Photomultiplern wird der Unterschied der Intensitäten zwischen dem Sauerstoffmultiplet bei 7772/5 Å und dem benachbarten Untergrund gemessen. Der entsprechende Spannungsunterschied wird auf einem digitalen Voltmeter angezeigt und automatisch

ausgedruckt. Es werden pro Probe 2.5 Min benötigt. Die Empfindlichkeit beträgt 1 μg O. Der Variationskoeffizient variiert zwischen 6–15% und ist von der Homogenität der Probe abhängig.

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A HIGH RESOLUTION MASS SPECTROMETRIC MEASUREMENT SYSTEM FOR A VACUUM FUSION APPARATUS*

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Mass spectrometers can be used for the analysis of gas mixtures in dynamic as well as static systems. They have been employed in various ways for the assay of gases in metals[1-3], but they have not been fully utilized with the vacuum fusion extraction method for assaying oxygen and nitrogen in metals. Although high vacuum is a requisite in both mass spectrometry and vacuum fusion, direct application of the mass spectrometer has been handicapped because oxygen and nitrogen are normally extracted in the form of carbon monoxide and molecular nitrogen, both having nominal masses at 28 but differing by about 0.011 mass units. Higher than usual resolution (1/2500) is required of the mass spectrometer if the resulting gas mixture is to be assayed directly using parent ions, which gives the highest sensitivity. In previous applications the lack of instrumental resolution has been circumvented by various means with loss of sensitivity, lengthened analysis time, and/or increased complexity of the analysis program.

This paper describes experiments in which a high resolution mass spectrometer was employed for assaying gas mixtures extracted from metals by means of a vacuum fusion apparatus. The total amount of the gases evolved from a sample was pumped through the mass spectrometer ion source. The parent ions of carbon monoxide and nitrogen were employed in the assay. This scheme allows rapid, sensitive, and simultaneous determinations of carbon monoxide and nitrogen as well as indication of any possible hydrocarbon contamination. The data are displayed in a manner similar to that described by FEICHTINGER *et al.*[4] in which a "gas-evologram" was obtained with a vacuum gas gauge and a chromatograph for gases extracted from metals in a vacuum fusion apparatus.

EXPERIMENTAL

Gas extraction apparatus

The resistance furnace assembly in the vacuum fusion apparatus was similar to that described by COOK AND SPEIGHT[5] except that the graphite shield was eliminated in order to reduce the amount of outgassing. The furnace and crucible assembly

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* Contribution No. 1624. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

was first outgassed at 1600° and then the temperature was lowered to an operating value of 1300°. Pure tin and silver metal samples were analyzed using a molten tin bath in a graphite crucible. The operating temperature of 1300° was found sufficient for complete extraction of oxygen and nitrogen from tin and silver. Comparison of our results with those obtained at various temperatures on a commercial (National Research Corp., type 912) vacuum fusion gas analysis apparatus confirmed the fact of complete extraction at these operating conditions.

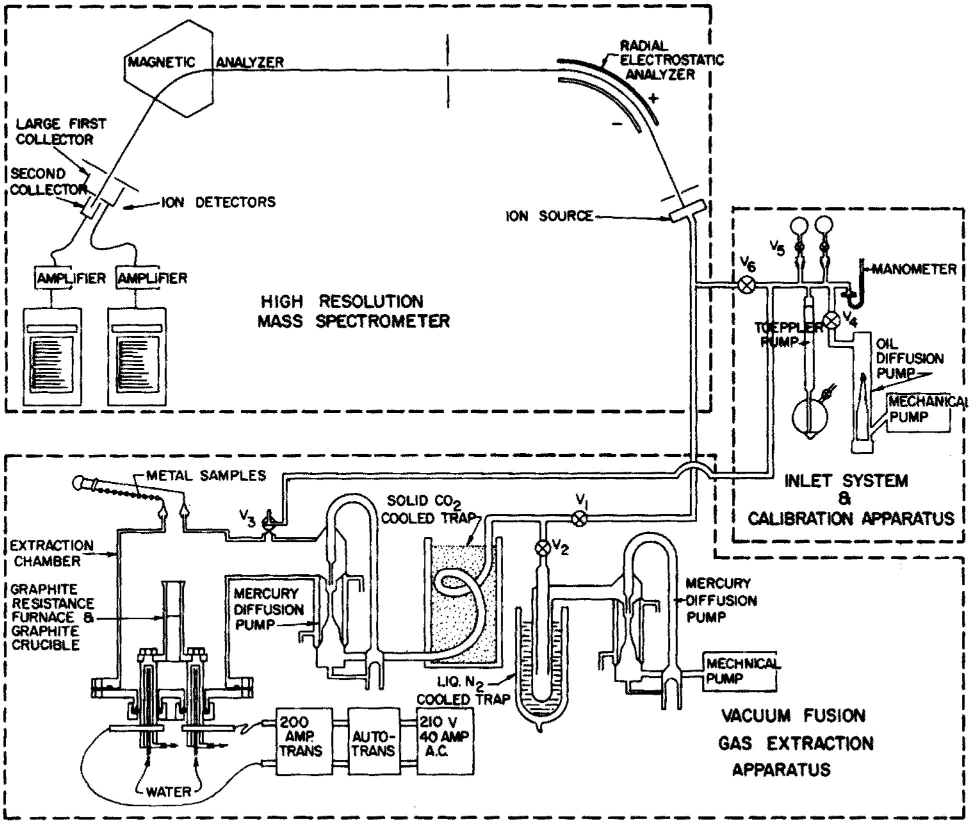

Fig. 1. Schematic drawing of a high resolution mass spectrometric measurement system for a vacuum fusion analysis.

A schematic diagram of the apparatus is shown in Fig. 1. An autotransformer and stepdown transformer with a 200-A secondary supplied the furnace power. Furnace resistance was 0.08 ohms. Pumping of the evolved gas from the extraction chamber was accomplished with a mercury diffusion pump in series with a small solid carbon dioxide-cooled glass cold trap (necessary to keep mercury out of the mass spectrometer when valve V_1 was open). Initial evacuation and outgassing of the gas extraction apparatus was through V_2 into a separate vacuum system consisting of a liquid nitrogen-cooled trap, a second diffusion pump, and a mechanical fore pump. Sample analysis was performed with V_2 closed and V_1 open. Valve V_3 allowed for injection of a standard gas aliquot into the furnace region for calibration purposes. Provisions were made to handle 12 successive metal samples in the gas extraction chamber.

Mass spectrometer

The high resolution mass spectrometer was constructed at these laboratories and has been described in detail[6]. The double-focusing optics were according to the theory of JOHNSON AND NIER[7]. The radial electrostatic analyzer had a 70° sector with a mean radius of 4.123 in. A 0.0017-in. slit, which limited the values of α and β in the equation describing the ion optics, was located at the image of the electrostatic analyzer. The magnetic analyzer was a 60° sector with a 3-in. radius of curvature. The ion source was a Nier type whose operating conditions had been modified to increase sensitivity when used with slits of reduced width[8]. The width of the object slit in the source was 0.0004 in. The mass spectrometer ion detection system consisted of dual collectors[9] such that the collectors could be used individually or simultaneously. Electrometer amplifiers with $4 \cdot 10^{10}$-ohm input resistors and 100% inverse feedback were employed. Strip-chart recorders were provided for each amplifier. Provisions were made for cyclic magnetic scanning of variable scan width and scan rate. The mass spectrometer was differentially pumped with a 8 l/sec (Varian Associates, Palo Alto, California) ion-pump on a source chamber and a liquid nitrogen cold trap followed by a two-stage mercury diffusion pump and mechanical pump on the analyzer chambers. Pressures of $2 \cdot 10^{-8}$ Torr in the source region and $1 \cdot 10^{-7}$ Torr in the analyzer sections were obtainable.

Sample analysis and calibration

Before sample introduction the ion beam in the mass spectrometer was focused to allow a cyclic scan (approximately 10 sec per scan cycle) of the 28 ± 0.10 mass region across the slit in front of the second collector. Ion currents due to CO^+,

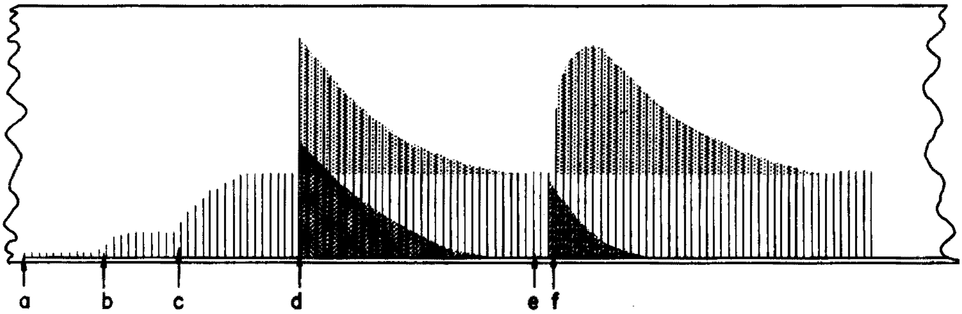

Fig. 2. Drawing of strip-chart recordings of ion currents during typical assays. Cyclic scan of mass 28 ± 0.1 region. (a) Signal due to residual CO in mass spectrometer. (b) V_1 is opened which increases signal slightly. (c) V_2 is closed which requires all gases from extraction chamber to enter mass spectrometer. (d) V_3 is turned to inject a known aliquot of CO and N_2 into the extraction chamber. (e) Signal returns to background level. (f) Metal sample is dropped into hot crucible yielding a CO^+ signal and a $C_2H_4^+$ signal.

N_2^+, and $C_2H_4^+$ were individually observable on the recording of the amplifier output of the second collector. The recording of the ion currents falling on the large, first collector yielded the sum of the CO^+, N_2^+, and $C_2H_4^+$ ion currents. A drawing representative of typical strip-chart recordings from the second collector is shown in Fig. 2 for the various valve settings, the standard gas aliquot injection, and the metal sample introduction. As may be observed in the Fig., the mass spectrometer pressure rose slightly when V_1 was opened and rose to a still higher steady background level when V_2 was closed. After the background reached a steady state (a pressure of approximately $1 \cdot 10^{-7}$ Torr in the mass spectrometer ion source region) a calibration gas aliquot was injected into the extraction chamber and the gases were assayed. After each "gas-evologram" was recorded and the ion current signals had returned to the background level, additional calibration aliquots could be injected or a metal sample could be dropped directly into the heated crucible and the evolved gases assayed. Calibration with the standard gas aliquot was performed by means of the three-way stopcock, V_3, and the regular mass spectrometer sample inlet system shown in Fig. 1. A reference gas mixture of known composition was introduced into the previously evacuated inlet system and the pressure (read on a closed end manometer) was adjusted by means of the Toeppler pump. Stopcock V_3 was turned 90° (counterclockwise from the illustrated position) thereby injecting an aliquot of the gas mixture corresponding to the internal volume of the stopcock into the gas extraction chamber. (The internal volume of the stopcock was measured to be 0.161 ± 0.002 ml in the present apparatus by weighing the stopcock, filling the internal volume with mercury and reweighing.) The standard gas aliquot injection yielded a "gas-evologram" whose area was directly proportional to the moles of gas within the internal volume of the stopcock. The "gas-evologram" areas were measured directly on the strip-chart recording with a compensating polar planimeter.

After all of the injected gas or the extracted gas had been pumped into the solid CO_2-cooled trap region, the ion current signal decreased toward the background level at a definite rate dependent upon the molecular gas flow-rate from the cold trap and through the ion source of the mass spectrometer. Since the rate of decrease was reproducible, the area under this portion of the "gas-evologram" curve could be determined generally without waiting for the ion current to return to the background level.

RESULTS

Results from the assay of silver by conventional volumetric vacuum fusion and mass spectrometric vacuum fusion are compared in Table I. The values are in good agreement. Sample sizes in the mass spectrometer analysis ranged from 0.030 to 0.170 g and no correlation between sample size and amount of oxygen found was observed. Sample size for the volumetric vacuum fusion measurements ranged from 0.356 to 0.452 g.

A series of comparisons was also made with tin capsules normally used for holding standards in a conventional vacuum fusion apparatus. The results are shown in Table II. Here a significant difference was observed between the two vacuum fusion methods in that the oxygen and nitrogen values were considerably higher from the conventional vacuum fusion apparatus. However a significant $C_2H_4^+$ ion current

TABLE I

ANALYSIS OF SILVER FOR OXYGEN AND NITROGEN

Conventional vacuum fusion analysis[a] *(Bath temp. 1300°)*			*Mass spectrometer vacuum fusion analysis (Bath temp. 1300°)*		
Trials	*O (p.p.m.)*	*N (p.p.m.)*	*Trials*[f]	*O (p.p.m.)*	*N (p.p.m.)*
1	107	<1	1[b]	103 ± 8	<1
2	103	2	2[c]	99 ± 7	<1
3	104	<1	3[d]	109 ± 9	<1
			Ave.[e]	103 ± 10	

[a] No estimate of the uncertainty available.
[b] Set of 4 samples (0.030 g to 0.077 g).
[c] Set of 8 samples (0.032 g to 0.093 g).
[d] Set of 7 samples (0.053 g to 0.169 g).
[e] All 17 samples used to obtain average.
[f] Each set of samples was assayed on different days.

TABLE II

ANALYSIS OF TIN FOR OXYGEN AND NITROGEN

Conventional vacuum fusion			*Mass spectrometer vacuum fusion*			
Trial[a]	*O (p.p.m.)*	*N (p.p.m.)*	*Trial*[b]	*O (p.p.m.)*	*N (p.p.m.)*	$C_2H_4^+$
1	72	7	1	29	<1	0.11[c]
2	103	5	2	32	<1	0.12
3	75	15	3	27	<1	0.14
4	75	5	4	29	<1	0.12
5	85	5	5	32	<1	0.12
6	109	12	6	30	<1	0.07
			7	32	<1	0.13
			8	28	<1	0.13
			9	26	<1	0.16
			10	27	<1	0.14
			Ave.	29		0.12
			5	2.4		0.02

[a] Trials 1, 2, 3 at 1300°; 4, 5, 6 at 1650°.
[b] All trials at 1300°.
[c] $C_2H_4^+$ signal is relative only. The value given represents the fraction obtained when the area under the $C_2H_4^+$ curve is divided by the area under the CO^+ curve.

signal was observed from these tin samples which was not observed with the silver or with the standard aliquot injections. These results indicate the possible error which will be encountered in the conventional apparatus when hydrocarbons are present.

In the conventional vacuum fusion apparatus the extracted gases are passed over copper oxide held at *ca.* 325° which oxidizes the carbon monoxide to carbon dioxide; next the gases are pumped through anhydrous magnesium perchlorate to remove water; then raising and lowering of the liquid nitrogen level on a cold trap allows separate manometric measurement of the oxygen and nitrogen as CO_2 and N_2. In this procedure any methane present would indicate erroneous values for nitrogen whereas higher boiling hydrocarbons would indicate erroneous values for oxygen in the sample. This problem is not encountered with the mass spectrometer since the

TABLE III

CALIBRATION OF THE APPARATUS USING ARTIFICIAL GAS MIXTURES OF CO AND N_2 INJECTED AS STANDARD ALIQUOTS WITH V_3

Trial	*Mixture data*		*Pressure*[a] *(Torr)*	*Moles*[b] $\cdot 10^9$		*Area*[c] *in relative units*		*Calibration factor (moles* $\cdot 10^9$*/area)*	
	%CO	*%N_2*		*CO*	*N_2*	*CO*	*N_2*	*CO*	*N_2*
1	91.9	8.1	16.9	137.	12.0	0.115	0.053	1190	227
2	91.9	8.1	16.7	135.	11.9	0.109	0.037	1240	322
3	91.9	8.1	9.6	77.6	6.84	0.0683	0.028	1140	245
4	91.9	8.1	9.4	76.0	6.69	0.0696	0.024	1090	279
5	91.9	8.1	32.9	266.	23.4	0.252	0.107	897	219
6	91.9	8.1	32.0	259.	22.8	0.263	0.114	985	200
7	91.9	8.1	31.0	257.	22.3	0.253	0.110	1020	202
8	70.9	29.1	27.2	170.	69.6	0.118	0.241	1440	289
9	70.9	29.1	21.1	132.	54.0	0.0985	0.208	1340	260
10	70.9	29.1	19.0	118.	48.6	0.0971	0.200	1220	243
11	70.9	29.1	23.2	145.	59.4	0.125	0.246	1160	241
12	70.9	29.1	17.2	107.	43.8	0.0985	0.186	1090	235
13	45.8	54.2	18.3	73.7	87.3	0.0567	0.309	1300	282
14	45.8	54.2	15.2	61.2	72.5	0.0502	0.277	1220	262
15	45.8	54.2	43.5	175.	207.	0.137	0.761	1277	272
16	45.8	54.2	33.0	133.	157.	0.111	0.574	1200	274
17	45.8	54.2	24.9	100.	119.	0.0837	0.436	1200	273
18	45.8	54.2	18.1	72.9	86.3	0.0614	0.315	1190	274
19	45.8	54.2	12.9	52.0	61.5	0.0447	0.217	1160	283
20	45.8	54.2	9.1	36.6	43.4	0.0323	0.147	1130	295
21	45.8	54.2	6.9	27.8	32.9	0.0241	0.105	1150	313
22	96.5	3.5	12.9	110.	3.92	0.107	0.017	1050	230
23	96.5	3.5	11.6	98.6	3.53	0.0871	0.010	1130	350
24	96.5	3.5	10.0	85.0	3.04	0.0758	0.008	1120	380
							Ave.	1160	269
							σ	115	25

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[a] Total pressure of CO and N_2 in the internal volume of V_3.

[b] Obtained from gas mixture percentages (column 2 and 3), pressure (column 4), and a volume of V_3 (0.161 ml).

[c] Measured with a planimeter on the recorded chart paper.

oxidation step of the standard procedure is unnecessary and the CO^+, N_2^+, and $C_2H_4^+$ ion current signals are a direct measure of the individual gases.

Calibration with different mixtures of CO and N_2 is illustrated in Table III. The different mixtures given in column 1 were prepared in a precision gas-mixing apparatus. The standard deviation of the calibration factor (moles of gas injected per unit "evologram" area generated) is given in the lower right hand corner. The sensitivity of the apparatus may be judged from the smallest samples in the Table. The sensitivity of this method of vacuum fusion gas analysis is dependent upon the variation in flow rate from the extraction chamber and through the mass spectrometer. This was measured to be approximately $1.4 \cdot 10^{-8}$ g of oxygen in 6 min for the present apparatus. This figure is based on the fact that during this period of time, a sample containing 1.3 μg of oxygen yielded an area 94 times greater than the sum of all the areas generated by the random fluctuations of the background signal. The time required for an analysis is limited mainly by the extraction time since the data are recorded as the gas is evolved from the heated graphite crucible.

DISCUSSION

A high resolution mass spectrometer can be applied to the direct analysis of gases evolved in a vacuum fusion apparatus. All of the evolved gas is pumped through the mass spectrometer ion source yielding a high analytical sensitivity and reducing the complexity of the analytical procedure. The requirement of determining and subtracting a blank is circumvented by using a dynamic gas flow system. The calibration procedure is simple. Assay of samples containing greater or lesser amounts of oxygen and nitrogen than those reported here (0.45 to 17.0 μg oxygen and 0.08 μg to 5.8 μg nitrogen) should be straightforward. Quantitative correction for hydrocarbon impurities is possible. Analysis time is limited by the time required to extract the gas from the sample. The accuracy attained in these experiments was $\pm$ 10%. However, an important fact which deals with the particular mass spectrometer used here must be emphasized. The small α- and β-limiting slit located at the image of the electrostatic analyzer through which the ion beam passes requires one to maximize manually the signal for large changes in ion beam intensities. The precision would have been increased considerably if this slit were not present. The slit is however necessary in this small double-focusing mass spectrometer in order to achieve the required high resolution. However, in mass spectrometers with larger design parameters, high resolution can be achieved without the slit.

An implied requirement for adaptation of a gas extraction system to this type of mass spectrometric analysis is that the flow rate due to outgassing of the furnace must be within the capability of the mass spectrometer vacuum system to maintain normal operating pressures.

SUMMARY

A high resolution mass spectrometric read-out system for a vacuum fusion apparatus is described. Rapid analyses are possible and the rate at which various gases are evolved can be monitored. Gas mixture assays are accomplished by scanning the nominal mass 28 peak. Serial measurements of CO^+, N_2^+ and $C_2H_4^+$ are made. Thus detection and measurement of evolved hydrocarbons are possible. The results for silver and tin from a conventional vacuum fusion apparatus and the mass spectrometer apparatus are compared.

RÉSUMÉ

Les auteurs décrivent un système de mesure spectrométrique de masse de grand pouvoir séparateur pour appareil de fusion dans le vide. Des analyses rapides sont possibles; des mesures de CO^+, N_2^+ et $C_2H_4^+$ ont été faites. Il est ainsi possible d'effectuer détection et dosage d'hydrocarbures. Les résultats, obtenus pour l'argent et l'étain, avec l'appareil conventionnel de fusion dans le vide et le spectromètre de masse, sont comparés.

ZUSAMMENFASSUNG

Es wird eine hochauflösende Massenspektrometeranordnung für Vakuumaufschlussapparaturen beschrieben. Schnelle Analysen sind möglich. Die Geschwindigkeit mit der verschiedene Gase entwickelt werden, kann bestimmt werden. Es wurden Reihenuntersuchungen von CO^+, N_2^+ und $C_2H_4^+$ durchgeführt. Der Nachweis und die Messung entwickelter Kohlenwasserstoffe ist möglich. Die Ergebnisse für Silber und Zinn mit einer konventionellen Vakuumaufschlussapparatur und dem Massenspektrometer werden miteinander verglichen.

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ELECTRON-TRANSFER REACTIONS OF THE HALOGENS AND THEIR COMPOUNDS

PART II. LIMITING CONDITIONS FOR THE QUANTITATIVE REACTION OF BROMATE WITH ARSENIC(III) AND ANTIMONY(III)

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A number of investigations[1-3] have followed GYÖRY's introduction[4] of bromate as a titrant for arsenic(III) and antimony(III). A kinetic study[5] showed that negative errors in the determination of antimony(III) in 0.22 to 1.0 *M* hydrochloric acid initially free from bromide arose from induced air oxidation of antimony(III). Positive errors were found at low and high acid concentrations[5]. SMITH[3] has made the empirical observation that the titration is satisfactory when 15 to 35% by volume of concentrated hydrochloric acid is present at the equivalence point. KEW *et al.*[6] give an effective range of 1.2 to 3.5 *M* hydrochloric acid for the accurate determination of arsenic(III) at 80° without added bromide when methyl orange is used as indicator, and report sluggish indicator response outside this range. The stoichiometry and velocity of the reactions have had little attention; this investigation seeks more precisely to define the range of conditions for which the titrations are accurate by visual and potentiometric methods, and to discover the reasons for non-stoichiometry under unfavourable conditions.

EXPERIMENTAL

Reagents

0.05 M Arsenic(III). Dissolve 0.05 mole, accurately weighed, of AnalaR arsenious oxide, previously dried at 120° for 3 h, in 80 ml of warm 2.5 *M* AnalaR sodium hydroxide, add 80 ml of 5 *M* AnalaR hydrochloric acid and make up to 2 l, giving a resultant free acid concentration of approximately 0.1 *M*.

Other solutions and reagents were described previously[5].

Procedures

Standardisations. The reductant solutions were standardised against 0.01667 *M* bromate under established optimum conditions, using rosaniline hydrochloride as the indicator as previously described[5]. Agreement between experimental and calculated titres was invariably better than ±0.05%.

Kinetic measurements. The method was described previously[5]. Reactions were conducted in 250-ml graduated flasks immersed in a tank of water thermostatted to ±0.02°.

RESULTS AND DISCUSSION

Media 0.1 M in bromide

With the initial addition of sufficient bromide to give a concentration of 0.1 *M* at the equivalence point, and with the visual indicator, rosaniline hydrochloride, both arsenic(III) and antimony(III) gave closely similar plots of error *vs.* the hydrochloric acid concentration at the equivalence point (Fig. 1, curves A and D). The titration was quantitative at acid concentrations between 0.3 and 2.5 *M*, but suffered increasing positive errors as the concentration diverges beyond these limits.

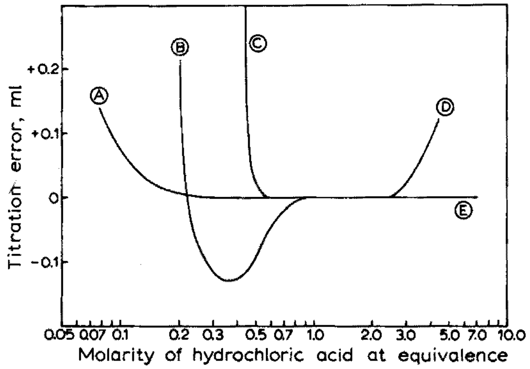


Fig. 1. Errors in the titration with 0.01667 *M* bromate of *ca.* 2.5 mmole of antimony(III) or arsenic(III) in media of various hydrochloric acid concentrations. Curve A, arsenic(III) or antimony(III) in 0.1 *M* bromide; curve B, antimony(III) in media initially free from bromide; curve C, arsenic(III) in media initially free from bromide. Curves A, B and C apply to both visual and potentiometric indication. Curve D, visual indication in media initially free from or containing bromide; curve E, potentiometric indication, maximum acid concentrations as shown in Table II.

With potentiometric indication (bright platinum — saturated calomel, E.I.L. 39A electrometer pH meter), positive errors again resulted at acid concentrations below 0.3 *M*, but the upper limiting concentration was extended for arsenic(III) at least as far as 6.52 *M*, at which the potential change through equivalence was still large and abrupt (Fig. 2A). For antimony(III), the increasing reductant potential as the acid concentration increased approached the bromine potential so that while the curve was acceptable and the accuracy good at 4.0 *M*, the curve was poor at 5.0 *M*, and the titration became impossible at 6.5 *M* (Fig. 2B); thus the upper limit of acid concentration for quantitative results must be set at 4.0 *M*.

The positive errors at acid concentrations above 2.5 *M* (Fig. 1, Curve D) must therefore be ascribed to the indicator and not to the reaction. The indicator (I) functions by polybromination (up to penta) of the positions ortho- to the amino

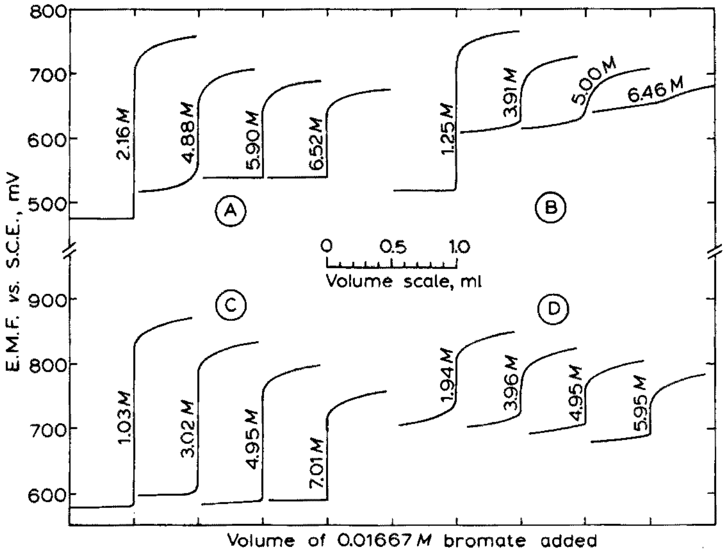
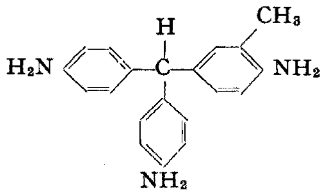


Fig. 2. Potentiometric titrations with 0.01667 M bromate of *ca.* 2.5 mmole of arsenic(III) or antimony(III). Hydrochloric acid concentrations at the equivalence point are as shown on the curves. Group A, arsenic(III) in 0.1 M bromide; B, antimony(III) in 0.1 M bromide; C, arsenic(III) in media initially free from bromide; D, antimony(III) in media initially free from bromide.



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groups, and as the acid concentration rises, the amino groups become successively protonated, upon which the rate of bromination of the cationic forms of the indicator decreases rapidly and the indicator response becomes sluggish leading to over-titration.

Both visual and potentiometric methods gave positive errors at acid concentrations below 0.3 M, and an explanation must be sought in the kinetics of the reactions.

Rate constants and energies of activation. The reactions are all zero order in reductant concentration, and, as in the case[5] of antimony(III), obey the fourth-order rate law,

$$-\mathrm{d}[\mathrm{Red}]/\mathrm{d}t = -\mathrm{d}[\mathrm{BrO_3^-}]/\mathrm{d}t = k_4[\mathrm{BrO_3^-}]\,[\mathrm{H^+}]^2[\mathrm{Br^-}]$$

where Red is the reductant. At acid concentrations less than 0.3 M, the rates are conveniently measurable, and in 0.1 M bromide the amount of bromide produced by the reaction does not significantly affect the bromide concentration, while the hydrogen ion produced in the oxidation of arsenic(III), antimony(III) and hydrazine exactly balances the amount consumed by the oxidant, so that $[\mathrm{H^+}]$ is invariant. The rate constant measured under these conditions is therefore the pseudo first-order constant k_1,

$$-\,\mathrm{d[Red]}/\mathrm{d}t = k_1[\mathrm{BrO_3^-}]$$

Determinations under exactly similar conditions gave the results shown in Table I. The figures for hydrazine are included in this paper for comparison; the remaining work on the stoichiometry will be reported in a later communication. The arsenic(III) and hydrazine sulphate solutions were neutralised to pH 7 before use, and an additional 1 g of tartaric acid was added to the antimony(III) solution to prevent hydrolysis. The tartrate does not affect the rate constant[5] and changes the hydrogen ion concentration by less than 1%. The agreement between the antimony and hydrazine results is excellent. The slightly lower value for arsenic is ascribed to the slight withdrawal of hydrogen ions by the formation of unionised arsenious acids, an effect obviated in the case of antimony by the use of the tartrate complex.

TABLE I

REACTION OF INITIALLY $3.33467 \cdot 10^{-3}$ *M* BROMATE WITH REDUCTANTS IN 0.100007 *M* BROMIDE AND 0.0975 *M* HYDROCHLORIC ACID

Reductant	*Initial concentration (M)*	*k_1 at 25° (sec^{-1})*
Sb(III)	$1.0004 \cdot 10^{-2}$	$3.183 \cdot 10^{-2}$
As(III)	$1.0004 \cdot 10^{-2}$	$2.702 \cdot 10^{-2}$
N_2H_4	$5.002 \cdot 10^{-3}$	$3.195 \cdot 10^{-2}$

The reaction is therefore independent of the nature of the reductant, and is controlled by the rate-determining step in the generation of the active oxidising species, Br_n^{2-n} under these conditions, from bromate, for which the absolute fourth-order rate constant, calculated from the antimony and hydrazine results, is 201.3 mole^{-3} min^{-1}. This is in substantial agreement with the value of 200 mole^{-3}min^{-1} obtained by SKRABAL AND WEBERITSCH[7] for the reaction conducted in the absence of reductant.

The plot of log k_1 against $1/T$ over the temperature range 20 to 40° was slightly curved, and gave a mean value of 14,760 cal mole^{-1} for the activation energy. YOUNG AND BRAY[8] gave the value of 16,000 cal mole^{-1} for the oxidation of hydrogen peroxide with bromate.

At low acid concentrations, therefore, the production of active oxidising species, governed by the slow fourth-order reaction step[5,9,10],

$$\mathrm{BrO_3^-} + \mathrm{Br^-} + 2\,\mathrm{H^+} \rightarrow \text{oxidising species} \qquad (1)$$

slows down so that an excess of bromate must be added to generate sufficient active oxidant to cause a response from the indicating system. Positive errors therefore arise.

Media initially free from bromide

Without the initial addition of any bromide, and with the visual indicator, rosaniline hydrochloride, positive errors arose at acid concentrations below 0.55 *M* in the determination of arsenic(III) (Fig. 1C) and below 0.22 *M* in the determination of antimony(III) (Fig. 1B), and above 2.5 *M* in both determinations. Once again, potentiometric titrations showed the upper limit to be a function of the indicator, bromination slowing down and eventually ceasing with progressive protonation of the indicator as the acid concentration rose.

The negative errors in the determination of antimony(III) in the acid concentration range 0.22 to 1.0 M and when the bromide concentration at the equivalence point was less than 0.004 M, were common to all methods of indication, and arose from induction of air oxidation of antimony(III) by the slow step in the generation of the active oxidant from the bromate[5].

With potentiometric indication (Fig. 2D), the increase in oxidant potential caused by diminution of the bromide concentration from 0.1 M to that produced by reduction of bromate, permitted the accurate determination of antimony(III) at acid concentrations up to 6.0 M. The determination of arsenic(III) (Fig. 2C) remained accurate at acid concentrations at least as high as 7.0 M. The lower limits of acid concentration were the same as for visual indication.

The positive errors at low acid concentrations arose from the same cause as before, the rate-controlling generation of the active species. Initially, this is reaction (2),

$$BrO_3^- + Cl^- + 2\,H^+ \rightarrow \text{oxidising species} \qquad (2)$$

the probable products being chlorine and bromine monochloride[11], but when a sufficient bromide concentration has been built up among the reaction products, reaction (1) takes over. Reaction (1) is considerably faster than reaction (2). The incidence of reaction (2) is characterised by an induction period lasting until sufficient bromide has been generated for the establishment of the normal kinetics of reaction (1). This induction period is greatly extended by the addition of mercuric chloride, which, by the formation of the more stable mercury(II) bromide, limits the concentration of free bromide ion, *e.g.* in 0.1 M hydrochloric acid and 0.1 M mercury(II) chloride a twentyfold reduction in bromide concentration occurs. The slow reaction at low acid concentrations leads to over-titration of arsenic(III) and antimony(III). Although in general agreement, the reaction of hydrazine shows several peculiarities, which will be reported in a later communication.

CONCLUSIONS

The titrimetric reaction of bromate with arsenic(III) and antimony(III) is stoichiometric and rapid under the conditions summarised in Table II, in which the concentrations refer to the equivalence point.

TABLE II

LIMITS OF HYDROCHLORIC ACID CONCENTRATION FOR STOICHIOMETRIC REACTION

Reductant	*Method of indication*	*Hydrochloric acid concentration ranges (M)*	
		Initial bromide concentration	
		0.1 M	*Zero*
Arsenic(III)	Visual	0.3 to 2.5	0.55 to 2.5
	Potentiometric	0.3 to >6.5	0.55 to >7.0
Antimony(III)	Visual	0.3 to 2.5	1.0 to 2.5
	Potentiometric	0.3 to 4.0	1.0 to 6.0

The reaction is independent of the nature of the reductant, has an absolute fourth-order rate constant of 201.3 mole^{-3} min^{-1} at 25°, and an energy of activation of 14,760 cal mole^{-1}, and displays an induction period in media having a bromide concentration of less than 0.004 *M* before normal kinetics is established. At acid concentrations below 0.22 *M* (antimony(III)) or 0.55 *M* (arsenic(III)) in media initially free from bromide, and below 0.3 *M* in media containing excess bromide, positive errors arise because of the slow liberation of active oxidising species. Induced air oxidation of antimony(III) during the induction period occurring when the initial bromide concentration is less than 0.004 *M*, causes negative errors at hydrochloric acid concentrations of 0.22 to 1.0 *M*. Positive errors with visual indication arise at hydrochloric acid concentrations above 2.5 *M* because of inhibition of the bromination of the cationic forms of rosaniline. Very high acid concentrations are permissible in the potentiometric determination of arsenic(III), but the coalescence of oxidant and reductant potentials with increasing acid concentration limits the permissible range for the antimony(III) reaction.

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SUMMARY

The limits of hydrochloric acid concentration within which the titrimetric determination of antimony(III) and arsenic(III) with bromate is quantitative within the normal precision of careful volume measurement (0.04%), are defined for both visual indication with rosaniline hydrochloride and potentiometric indication, in media initially containing no or 0.1 *M* bromide. These reactions are independent of the nature of the reductant, the rate-controlling step being the fourth-order reaction producing the active oxidising species. Rate constants and energy of activation were determined. The kinetic and potentiometric investigations were used to elucidate the origins of the errors arising under conditions outside the ranges of quantitative reaction.

RÉSUMÉ

Les auteurs ont examiné les limites de concentrations en acide chlorhydrique pour le dosage titrimétrique de l'antimoine(III) et de l'arsenic(III) au moyen de bromate. Elles sont définies, soit par indication visuelle avec chlorhydrate de rosaniline, soit par indication potentiométrique, avec ou sans bromure. Les constantes de vitesse et l'énergie d'activation ont été déterminées. Les recherches cinétiques et potentiométriques ont été faites pour trouver l'origine des erreurs se produisant en dehors des limites de la réaction quantitative.

ZUSAMMENFASSUNG

Die Grenzen der Salzsäurekonzentration, in der die massanalytische Bestimmung von Antimon(III) und Arsen(III) mit Bromat quantitativ ist, wurde sowohl für die visuelle Anzeige mit Rosanilinhydrochlorid als auch mit potentiometrischer Anzeige festgelegt, und zwar innerhalb der normalen Genauigkeit einer sorgfältigen

Volumenmessung (0.04%) und in einem Medium, das entweder anfangs kein Bromid enthielt oder 0.1 *M* an Bromid war. Die Reaktionen sind unabhängig von der Natur des Reduktionsmittels. Der geschwindigkeitsbestimmende Schritt ist eine Reaktion 4. Ordnung, die die aktiven oxydierenden Spezies hervorruft. Die Geschwindigkeitskonstanten und die Aktivierungsenergie wurden bestimmt. Die kinetischen und potentiometrischen Untersuchungen wurden benutzt, um die Fehlerursachen, die unter Bedingungen ausserhalb des Bereiches der quantitativen Reaktion entstehen, zu erläutern.

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A CRITICAL ANALYSIS OF THE STATISTICAL EFFECT IN METAL-COMPLEX FORMATION

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Interpretation of pH titration curves of polyacids and of formation curves of complex ions is facilitated by information about necessary relationships between the observable macroscopic equilibrium constants and the microscopic equilibrium constants involving all different species in solution.

For linear polyacids it is convenient to think of a polymer skeleton to which are attached many identical, distinguishable combining sites for protons. For this case a simple relationship between macroscopic and microscopic equilibrium constants can be obtained, based on the statistical distribution of protons on these sites[1]. Interaction between sites is treated separately. Justification for considering the sites as individually distinguishable is that the sites are in principle numberable, since they are connected in a specific order by the covalent bonds of the molecular skeleton. Stepwise reaction of a metal ion with ligand molecules has been treated in much the same manner by BJERRUM[2] and by SEN[3].

There are, however, fundamental differences between linear polyacids and complex ions. The number and the position of binding "sites" depends on the particular ligand, and site rearrangement may occur as ligands successively replace coordinated solvent molecules. There is a serious problem in deciding whether sites are distinguishable.

Proton binding on linear polyacids can be treated unambiguously by writing all possible microscopic equilibrium constants and the equations for conservation of mass. If all microscopic equilibrium constants are assumed equal, these equations can be combined to give the macroscopic equilibrium constants in terms of a single intrinsic equilibrium constant and a statistical factor. This cannot be simply done for the complex-ion case. Evaluation of the statistical factors for complex-ion formation requires mechanistic arguments. It is the purpose of this communication to demonstrate that the numerical value of the statistical factors is markedly dependent on the particular mechanistic model chosen. It is concluded that the concept of distinguishable, non-interacting sites is not as useful a concept for interpretation of complex-ion equilibria as has previously been suggested. The situation will be examined in detail for the case of a square-planar complex.

Formation of a square-planar complex

A set of stepwise macroscopic equilibrium constants for the reactions can be defined in terms of concentrations as

$$\begin{array}{ll} B + X \rightleftharpoons BX_1 & K_A = (BX_1)/(B)\,(X) \\ BX_1 + X \rightleftharpoons BX_2 & K_B = (BX_2)/(BX_1)\,(X) \\ BX_2 + X \rightleftharpoons BX_3 & K_C = (BX_3)/(BX_2)\,(X) \\ BX_3 + X \rightleftharpoons BX_4 & K_D = (BX_4)/(BX_3)\,(X) \end{array}$$

where B is the central metal ion, X is the ligand, and the quantities (X), (B), (BX_1), ..., (BX_4) are total concentrations of all species of the indicated composition.

There is but one geometric isomer and thus but one distinguishable species corresponding to each of the formulas B, BX_1, BX_3 and BX_4. However, BX_2 can exist in both *cis* and *trans* forms. The quantity (BX_2) is thus the sum of the concentrations $(cisBX_2)$ and $(transBX_2)$. Microscopic equilibrium constants and corresponding equilibria are

$$\begin{array}{ll} B + X \rightleftharpoons BX_1 & K_1 = (BX_1)/(B)\,(X) \\ BX_1 + X \rightleftharpoons cisBX_2 & K_2 = (cisBX_2)/(BX_1)\,(X) \\ BX_1 + X \rightleftharpoons transBX_2 & K_3 = (transBX_2)/(BX_1)\,(X) \\ cisBX_2 + X \rightleftharpoons BX_3 & K_4 = (BX_3)/(cisBX_2)\,(X) \\ transBX_2 + X \rightleftharpoons BX_3 & K_5 = (BX_3)/(transBX_2)\,(X) \\ BX_3 + X \rightleftharpoons BX_4 & K_6 = (BX_4)/(BX_3)\,(X) \end{array}$$

Macroscopic and microscopic equilibrium constant equations can be readily combined to yield

$$K_A = K_1,\ K_B = K_2 + K_3,\ K_C = K_4K_5/(K_5+K_4),\ K_D = K_6$$

This set of equations gives as much information as can be obtained without introduction of extrathermodynamic assumptions. With BJERRUM and SEN, it will be assumed that the rate of addition of X will be proportional to the number of available sites, and that the rate of removal of X will be proportional to the number of bound X. This assumption permits evaluation of equilibrium constant ratios for a particular detailed chemical model for complex formation. Two reasonable models will be considered.

Formation of square-planar ligand–metal complex from octahedral solvent–metal complex. If the solvated metal ion is an octahedral solvent–metal complex, then discussion of successive addition of ligands to yield a square-planar metal–ligand complex must take into account the fact that at least 2 ligand molecules are required together with the central ion to define a plane. There are thus 6 equivalent sites available for addition of X to B to give BX_1. There is just one way to dissociate the single X from a BX_1 ion. The equilibrium constant K_1 is thus proportional to 6/1. The proportionality constant K will be set equal to K_4, since K_4 must be proportional to 2/2.

It will be observed that the plane of the complex is defined in the species $cisBX_2$, BX_3 and BX_4, but not in $transBX_2$ in which the two ligands and the central ion are colinear. This model does not permit the formation of the species $cisBX_3$ in which no *trans* pair of ligands exists; incorporation of such a pathway into the model would change the derived statistical factor. With the help of Fig. 1, all microscopic equilibrium constants can be evaluated, giving

$$K_1 = 6K,\ K_2 = 2K,\ K_3 = (1/2)K,\ K_4 = K,\ K_5 = 4K,\ K_6 = (1/4)K$$

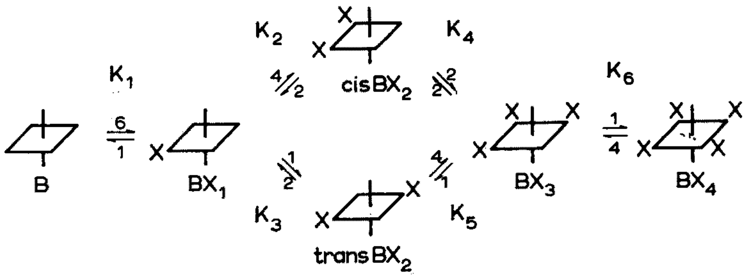

Fig. 1

The macroscopic constants are then

$$K_A = 6K, K_B = (5/2)K, K_C = (4/5)K, K_D = (1/4)K$$

Formation of square-planar ligand–metal complex from square-planar solvent–metal complex. In this mechanism it is assumed that the plane of the molecule is defined by the coordinated solvent molecules, as shown in Fig. 2. The microscopic equilibrium constants are

$$K_1 = 4K, K_2 = K, K_3 = (1/2)K, K_4 = K, K_5 = 2K, K_6 = (1/4)K$$

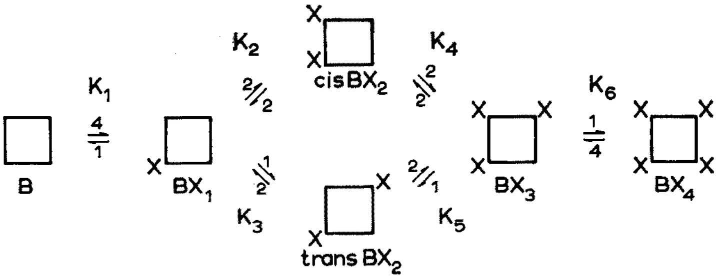

Fig. 2

This gives a set of macroscopic equilibrium constants as follows:

$$K_A = 4K, K_B = (3/2)K, K_C = (2/3)K, K_D = (1/4)K$$

This is the result given by both BJERRUM and SEN as the statistical effect in formation of a square-planar complex.

Discussion

Separation of factors influencing the relative magnitudes of successive formation constants introduces simplification when the sites are clearly defined and distinguishable. However, such is not the case for complex formation about a central metal ion, and here evaluation of a statistical factor involves the assumption of a particular mechanistic model. This is a dubious procedure at best, and it is particularly dangerous when a critical part of the mechanism, in this case the role of solvent, is poorly understood experimentally. It is certainly not possible in general to identify statistical effects which are independent of all other factors involved in determining the numerical values of the various equilibrium constants.

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SUMMARY

Evaluation of the statistical factor for formation of a metal–ligand complex requires explicit formulation of a detailed chemical model for the formation reaction. It is thus not possible in general to separate independent statistical effects from the other factors involved in determining the value of the equilibrium constants.

RÉSUMÉ

L'auteur a effectué une analyse critique de l'effet statistique dans la formation de complexes métalliques. Il n'est pas possible en général de séparer des effets statistiques indépendants d'avec d'autres facteurs intervenant lors de la détermination des constantes d'équilibre.

ZUSAMMENFASSUNG

Die Berechnung des statistischen Faktors zur Bildung eines Metall–Ligandkomplexes erfordert die explizite Formulierung eines detaillierten chemischen Modells für die Bildungsreaktion. Es ist im allgemeinen so nicht möglich unabhängige statistische Einflüsse von anderen Faktoren zu trennen, die in die Bestimmung der Werte von Gleichgewichtskonstanten eingeschlossen sind.

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) WITH ACID ALIZARIN BLACK S.N.

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In the course of an investigation of a series of copper(II)-selective metallochromic reagents, the production of an unusually stable and sensitive spectrophotometric reaction was observed between the bishydroxytrisazo dyestuff, Acid Alizarin Black S.N. (AABSN, CI Mordant Black 25), and copper(II) ions over a wide range of pH. The complex formed is sufficiently strong to resist breakdown by EDTA, which can, therefore, be used as a mass-masking agent to prevent the interference of most of the many ions which react metallochromically with the reagent. The freedom from interference, stability of the complex and sensitivity of the colour reaction prompted us to undertake a study of the nature of the two complexes formed between copper(II) and the reagent and to devise an analytical procedure. AABSN has already been used, *inter alia*, as a particularly sensitive EDTA indicator for calcium in dilute solution[1], and as a spectrophotometric reagent for calcium[2] and for thorium[3].

Examination of absorption spectra

The absorption spectra in Fig. 1 show that copper(II) forms two complexes with AABSN. A 1 : 1 purple complex is formed with an absorption maximum at 590–595 mμ whilst the reagent itself shows a considerably more intense band peaking at 650 mμ. With a 2 : 1 molar ratio of copper to AABSN a differently coloured complex is formed with a band showing maximum absorption over the spectral range 515–565 mμ and a lesser band at 435 mμ. It can also be seen that an appreciable amount of the 1 : 1 species still shows in the band at 595 mμ. Figure 2 shows the same spectra, obtained in the presence of an excess of EDTA. It can be seen that the purple 1 : 1 complex is still formed, but with the absorbance maximum at 605–610 mμ whilst the red 2 : 1 Cu–AABSN complex is not formed at all. In this instance the presence of the large amount of copper(II) shifts the maximum of the 1 : 1 band back to 590–595 mμ. Neither the band at 515–565 mμ nor that at 435 mμ is in evidence. Thus the presence of a substantial excess (× 10) of EDTA has little effect on the formation of the strong 1 : 1 Cu–AABSN complex, but it completely suppresses the 2 : 1 Cu–AABSN complex.

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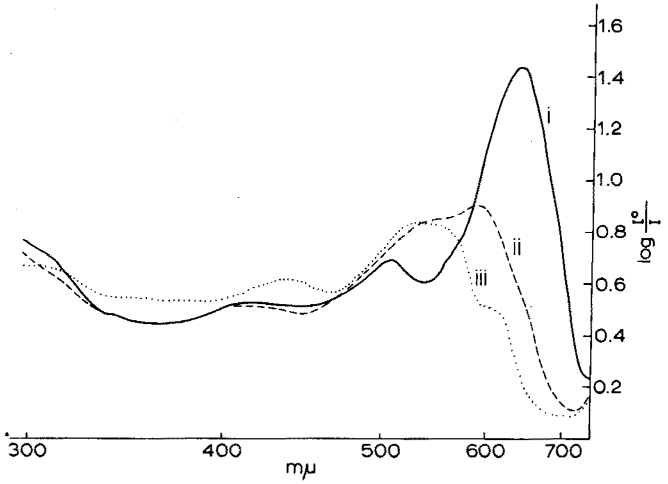

Fig. 1. Absorption spectra. (i) 5 ml 10^{-4} *F* AABSN + NH_3 (5 ml of 0.88 s.g.) in 100 ml. 1-cm cuvette against H_2O. Hilger "Ultrascan" spectrophotometer. (ii) As (i) but with 5 ml of 10^{-4} *F* Cu(II) solution present. (iii) As (i) but with 10 ml of 10^{-4} *F* Cu(II) solution present.

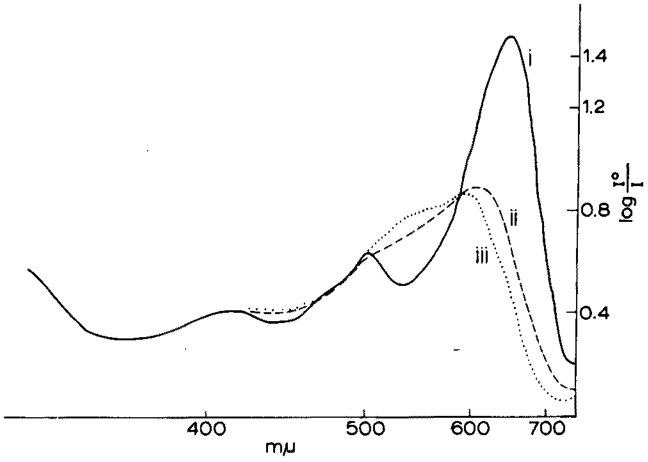

Fig. 2. Absorption spectra in presence of EDTA. (i), (ii) and (iii) as in Fig. 1, but with the addition of 2 ml of 10^{-2} *F* EDTA to each solution.

DEVELOPMENT OF ANALYTICAL METHOD

The optimum conditions for complex formation were established with respect to pH, time of development, stability of colour, nature of buffer, etc. Since only the 1 : 1 complex is formed when AABSN is present in excess, and since it is not broken down by an excess of EDTA, only the 1 : 1 complex was examined for analytical utility; its reactions were studied in the presence of a *ca.* 40-fold excess of EDTA.

The pH effect was first studied over the range pH 8.5–11.3 in the presence of glycine–sodium hydroxide buffers. Solutions around pH 11 showed maximum absorbance, but it became apparent that with the glycine–sodium hydroxide buffer the sensitivity was lower than with the ammonia medium used in earlier experiments. Incorporation of some ammonia in the glycine buffer restored the loss of sensitivity at the same pH. It appears from this evidence that ammonia may take part in the formation of the complex. Re-investigation of the pH dependence of the colour with an ammonia–glycine–sodium hydroxide buffer and a plot of pH *vs.* absorbance showed a horizontal zone of maximum absorbance over the pH range 11–11.4.

In the absence of EDTA, the time required for colour development in ammoniacal medium was found to be less than 10 min; in its presence a development time of 30 min was required and the absorbance remained unchanged thereafter for more than 24 h. A development time of 1 h was selected as a matter of convenience in subsequent studies.

Beer's law was tested over the range 6.5–32.5 μg of copper(II) in the presence of 2 ml of $10^{-2}F$ EDTA with 50 ml of $10^{-4}F$ AABSN. A straight line graph was obtained, the extension of which passed through the origin. The slope of this curve gave a molecular absorptivity of $\varepsilon_{650\ m\mu} = 28{,}000$, representing a sensitivity index of 0.0022 μg Cu/cm^2 according to SANDELL's definition. These measurements were made at 650 mμ following the decrease in the peak height of the reagent band rather than at the band maximum of the complex at 595–600 mμ where the absorbance of the reagent is almost identical. This is most easily effected, as described under EXPERIMENTAL, by measuring the absorbance of the blank solution against zero absorbance set with each test solution in turn.

Although it was not tested, there is little doubt that the Beer's law range of the method extends well beyond the upper limit of 32.5 μg of copper(II) used in these studies. The excess of reagent used at this point corresponds to 10-fold. Independent studies of the relationship between absorbance and excess of reagent revealed that this was a sufficiently great excess.

Interference studies were conducted with 33-fold gram-ionic excesses of some 20 cations and 6 anions (*i.e.* 33-fold relative to the 19 μg of copper(II) used in the tests). The amount of EDTA present was 2 ml of $10^{-2}F$ EDTA solution, *i.e.* more than enough to complex the foreign cations. At the stated level no interference was observed from Al, Be, Ca, Cd, Mg, Mn(II), Pb, Sb(III), Sr or Zn; some interference due to Cr(III), La(III), Ni, Sn(II) and Zr became vanishingly small when these were present in only 4-fold excess over copper(II). However, interference was still found from Bi, Co(II), Fe(III) and Th. Masking procedures for these ions proved to be unsuccessful and consequently these 4 cations must be removed before the proposed method can be applied.

Separation of *ca.* 100-fold (gram-ionic) amounts of iron, thorium, lanthanum and bismuth was readily achieved by the addition of 2 ml of saturated aluminium potassium sulphate solution as a carrier for their coprecipitation at pH 8.5, but as shown in Table I, cobalt still interfered by yielding high results. Attempts to use manganese dioxide as carrier proved equally ineffective in removing the interference of cobalt.

None of the anions examined, *viz.* fluoride, iodide, phosphate, tartrate or thioglycollate, interfered though all are known to form complexes or to react other-

TABLE I

REMOVAL OF INTERFERENCES BY COPRECIPITATION

(5 ml of $10^{-4}F$ Cu(II) + 1 ml of $10^{-2}F$ interfering cation)

Interfering ion	*Absorbance*	
	Before coprecipitation	*After coprecipitation*
—	0.142	0.142
Fe(III)	0.394	0.144
Th	2.0	0.146
La	0.262	0.147
Bi	0.268	0.146
Co(II)	1.990	0.950

wise with copper ions. Cyanide interfered seriously, however, and must be absent.

As a result of these studies it may be concluded that for the range of ions examined, there are no serious interferences that cannot be overcome by the masking action of EDTA or by application of a simple coprecipitation–collection technique, except those of cobalt(II) and cyanide.

EXPERIMENTAL

Reagents

Copper(II) sulphate $10^{-4}F$. Dissolve 0.2497 g $CuSO_4 \cdot 5H_2O$ (AR) in 1 l of water containing 1 ml of 0.5 *M* sulphuric acid. This solution ($10^{-3}F$) is diluted to give a $10^{-4}F$ standard solution as required.

Acid alizarin black S.N. $10^{-4}F$ *and* $10^{-3}F$. A sample of the commercially available dye was recrystallised twice from water and assayed by titanium(III) chloride titration; it was found to be 83% free acid. Sodium ash determination confirmed that the inert material present was sodium chloride. On the basis of this analysis, 0.1795 g of AABSN was dissolved in 250 ml of water to give a $10^{-3}F$ solution. A $10^{-4}F$ solution was obtained by proportionate dilution of the $10^{-3}F$ solution.

For routine analysis, the 50% pure (NaCl) dye may be used directly. A $10^{-4}F$ solution is then prepared by dissolving 0.128 g AABSN in 1 l of water. The reagent solution is quite stable.

Buffer pH 11.2. Dissolve 7.5 g of glycine, 5 g of sodium chloride and 15 ml of ammonia solution (s.g. 0.88) in distilled water, and dilute to 1 l after adjustment to pH 11.2 by addition of sodium hydroxide.

Apparatus

A Unicam SP 600 spectrophotometer operated from a 12-V stabilized transformer, was used with 1-cm cuvettes.

Procedures

Calibration curve. Transfer 1–5 ml of $10^{-4}F$ copper sulphate solution to 100-ml standard flasks and add 2 ml of $10^{-2}F$ EDTA (disodium salt) solution, 10 ml of pH

11.2 buffer and 50 ml of $10^{-4}F$ AABSN reagent to each. Dilute the contents of the flasks to 100 ml with deionised or glass-distilled water and allow to stand for 1 h. Set zero absorbance against each test solution and measure the absorbance of the blank solution against each one in turn in 1-cm cuvettes at 650 mμ.

Analytical method. Take an aliquot of the test solution containing not more than 35 μg of copper(II) and take it through the procedure described under *Calibration curve.*

Determination of Cu(II) in presence of Fe(III), Bi, La(III) and Th

The following method removes these elements which interfere in the above procedure.

To the solution containing copper(II) and any of the above ions in a volume of less than 10 ml, add 2 ml of saturated aluminium potassium sulphate solution, 5 ml of glycine/sodium chloride solution (7 g of glycine and 5 g of sodium chloride per l) and sufficient ammonia dropwise to bring the pH up to 8.5 as measured on a pH meter. Bring the solution to the boil and filter without suction on a small porcelain filter disc through a No. 1 Whatman filter paper. Wash the residue on the paper 3 times with a little hot water containing a few drops of glycine/sodium chloride solution. Treat the combined filtrate and washings with 2 ml of $10^{-2}F$ EDTA solution, adjust the pH to *ca.* 11, cool and transfer to a 100-ml flask. Add 5 ml of pH 11.2 buffer, 50 ml of $10^{-4}F$ AABSN, dilute to the mark and allow to stand for 1 h, etc.

NATURE OF METALLOCHROMIC COMPLEX

In examining the absorption spectra of AABSN and its copper complexes, an indication was obtained that 1 : 1 and 1 : 2 AABSN–copper(II) complexes were formed. The formation of the 1 : 2 complex is not observed under normal analytical conditions where an excess of reagent is used, but its formation otherwise is not unexpected in view of the structure of the AABSN molecule and the existence in it of two *o,o'*-dihydroxyazo complexing centres with a common hydroxyl group. To obtain further information, a series of continuous variation experiments was undertaken. Where the existence of more than one complex is expected, the formation of these is best monitored at wavelengths where each complex makes a unique contribution to the total absorbance of the solution, *i.e.* a contribution which is measurably different from the simultaneous contribution made at the same wavelength by other absorbing species in the solution.

An examination of the absorption spectra in Fig. 1 reveals that at 650 mμ it is possible to follow the behaviour of the AABSN since the contributions made by the suspected 1 : 1 and 1 : 2 AABSN–copper complexes are much smaller. At 600 mμ the 1 : 1 complex makes a substantial contribution whilst the 1 : 2 complex shows a much smaller contribution. At 590 mμ there exists an isosbestic point for the 1 : 1 AABSN/Cu complex and the reagent but the behaviour of the 1 : 2 complex is substantially different. Accordingly, the method of continuous variation was applied at each of these wavelengths with a series of solutions whose total overall concentration (Cu(II) + AABSN) was maintained at $5\,\text{ml} \cdot 10^{-3}F$. The pH was controlled at 11.2 with 10 ml of the glycine buffer, and the solutions were diluted to 100 ml and measured after a minimum development time of 30 min using 1-cm cuvettes. Measurements were made in each instance against distilled water (dotted lines on curves in Fig. 3) and the corrected curves (solid lines) were obtained in the usual way.

Figure 3a at 650 mμ shows a well defined maximum at the 1 : 1 ratio confirming the existence of the stable purple complex. No evidence is shown here for the 1 : 2 complex. This is hardly surprising since the ratio of absorbances between the reagent and the 1 : 1 complex on the one hand and between the reagent and the 1 : 2 complex on the other differs little, and not unexpectedly the more stable of the two complexes shows up.

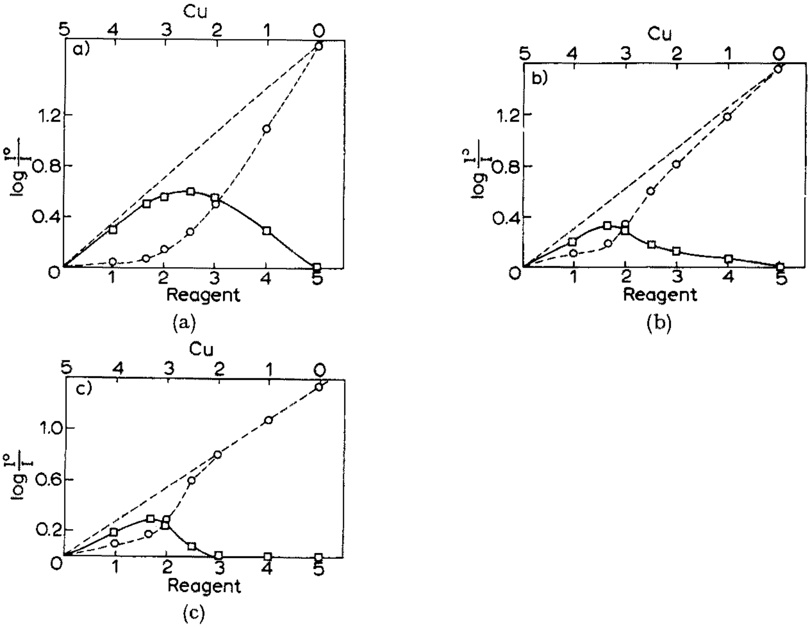

Fig. 3. Continuous variation experiments. (a) Varying concentrations of $10^{-3}F$ Cu(II) + $10^{-3}F$ AABSN (total 5 ml of $10^{-3}F$) + 10 ml pH 11.2 buffer. 100 ml volume, 1-cm cell measured at 650 mμ against water. Dotted line, actual plot; solid line, corrected plot. (b) As (a) but with measurement at 600 mμ. (c) As (a) but with measurement at 590 mμ.

Figure 3b at 600 mμ reverses these conditions. Here the ratio between the absorbances of the reagent and the 1 : 2 AABSN–copper complex on the one hand and the reagent and the 1 : 1 complex on the other is quite different, the difference being more pronounced for the 1 : 2 complex – AABSN system. Thus at 600 mμ a pronounced maximum is found corresponding to the 1 : 2 complex almost exactly, with a small break (minimum) corresponding to the 1 : 1 complex.

At 590 mμ (Fig. 3c), the isosbestic point for the 1 : 1 complex and the reagent, there is naturally no detectable formation of the 1 : 1 complex, but the 1 : 2 complex shows up quite clearly.

These data clearly reveal the formation of both 1 : 1 and 1 : 2 complexes. Since the data in Fig. 2 clearly reveal that a considerable excess of EDTA has a negligible effect on the curve for the 1 : 1 complex, no further continuous variation experiments were done to examine the effect of EDTA.

In the 1 : 1 complex it is very probable that the copper is held in the manner usually postulated for dihydroxymonoazo centres, by bonding with both the phenolic oxygens and one azo bond, probably with ammonia co-ordinated to the remaining position. In the 1 : 2 complex the copper can only be held by the other azo bond and by the remaining phenolic oxygen, unless a mesomeric sharing of electrons between the two copper atoms on the one hand and the (central) phenolic oxygen on the other is postulated. In either event, the stability of the 1 : 1 complex would be expected to be considerably greater than that of the 1 : 2 complex.

ANALYTICAL VALUE OF PROCEDURE

A very great number of reagents is available for the spectrophotometric determination of copper(I) and -(II) and the proposal of yet another reagent is only justified if it makes a substantial contribution. Table II shows the sensitivities of a

TABLE II

SPECTROPHOTOMETRIC METHODS FOR COPPER[4]

Cu(I) or (II)	*Reagent*	*Solvent medium*	*Wave-length (mμ)*	*Molar absorptivity ·10³*	*Interferences*
I	Cuproine	Isoamyl alcohol	546	6.43	CN^-, SCN^-, $C_2O_4^{2-}$, I^-
I	Neocuproine	Isoamyl alcohol	454	7·95	IO_4^-, NO_2^-, SCN^-, $Fe(CN)_6^{3-}$
I	Bathocuproine	Isoamyl alcohol	479	14.2	—
II	Dithizone	CCl_4	545	45	Pd, Au, Ag, Hg(I) and (II), Bi, Fe(III)
II	Dithizone	CCl_4	445	22.7	—
II	P.A.N.	Isoamyl alcohol	560	22	EDTA, CN^-
II	Diethyldithiocarbamate	Xylene	436	16.8	U, Mn, Bi, Co, Ni, Ce
II	Biscyclohexanone-oxalyldihydrazone	Water	595	16	Ni, Co
II	1,10-Phenanthroline	Water	272	34·5	—
II	1,10-Phenanthroline	Water	294	10.3	—
II	Fast Sulphon Black F	Water	630	14	Ni, Mn, Be
II	Salicylaldoxime	Amyl acetate	344	8.2	—
II	8-Hydroxyquinoline	Chloroform	410	5·2	Bi, Fe(III), Al, Ni, Co, In
II	8-Hydroxyquinoline	1 : 1 Benzene–CCl_4	400	4·7	Fe(III), Mo, V, etc.
II	α-Benzoinoxime	Chloroform	440	2.8	Ni and Co
II	Ammonia	Water	620	0.12	Ni, Co, etc.
II	AABSN	Water	650	28	CN^-, Bi, Co, Fe(III), Th, only in presence of EDTA

selection of the common reagents[4]. On the basis of sensitivity it will be seen that AABSN surpasses all other visible-range reagents except dithizone. The interference column in Table II is very incomplete, but even so it can also be seen that, whereas most reagents achieve selectivity by a (separative) extraction process, AABSN achieves its selectivity simply by the addition of a soluble masking agent to the aqueous solution. Moreover, the application of a separative process (coprecipitation) removes all the remaining cationic interference except that of cobalt. EDTA cannot be used with most of the other colorimetric reagents except for diethyldithiocarbamate (bismuth still interferes) because the copper complexes of these reagents are less stable than that with EDTA. The diethyldithiocarbamate extract is photochemically unstable.

On the grounds of sensitivity, stability, freedom from interference and ease of application AABSN appears to be a genuinely worthwhile reagent for the spectrophotometric determination of copper in the range down to 0.1 p.p.m.

One of us (M.H.) gratefully acknowledges the award of a Colombo Plan Scholarship and expresses his thanks to the Director, East Regional Laboratories, P.C.S.I.R., Dacca, East Pakistan, for granting leave of absence. We also thank B. AFGHAN (Imperial College) for independent checking of the procedure.

SUMMARY

Acid alizarin black SN (AABSN) gives a colour reaction with copper(II) in aqueous solution ($\varepsilon_{650} = 28{,}000$) which provides greater sensitivity than any other method in the visible range of the spectrum except dithizone. The complex is extremely stable, and EDTA can be used to mask most ions. Only Th, Bi, La(III), Fe(III) and Co(II) interfere seriously. The interference of the first 4 can readily be overcome by coprecipitation with aluminium hydroxide.

The nature of the two complexes formed between copper(II) ions and AABSN was examined by procedures of continuous variation.

RÉSUMÉ

Le noir d'alizarine acide S.N. donne une solution colorée avec le cuivre, en solution aqueuse ($\varepsilon_{650} = 28{,}000$), offrant dans le visible une sensibilité plus grande que n'importe quel autre réactif, à part la dithizone. Le complexe formé est extrêmement stable; EDTA peut être utilisé pour masquer la plupart des ions. Seuls Th, Bi, La et Co gênent sérieusement. Les quatre premiers peuvent être séparés par coprécipitation avec l'hydroxyde d'aluminium.

La nature des deux complexes formés par le cuivre(II) et AABSN a été examiné par des méthodes très distinctes.

ZUSAMMENFASSUNG

Saures Alizarinschwarz SN (AABSN) gibt in wässriger Lösung mit Kupfer(II) eine Farbreaktion ($\varepsilon_{650} = 28{,}000$), die eine grössere Empfindlichkeit verspricht als jede andere Methode im sichtbaren Bereich des Spektrums (ausser Dithizon). Der

Komplex ist extrem stabil. EDTA kann zur Maskierung der meisten Ionen verwendet werden. Nur Th, Bi, La(III), Fe(III) und Co(II) stören ernsthaft. Die Störungen der ersten 4 können durch Mitfällung mit Aluminiumhydroxid vermieden werden. Die Natur der zwei Komplexe, die zwischen Kupfer(II)-Ionen und AABSN gebildet werden, wurde untersucht.

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FRACTIONAL SUBLIMATION OF VARIOUS METAL ACETYLACETONATES

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Studies[1-4] carried out in this laboratory on the volatile characteristics of various metal β-diketone chelates have clearly indicated the possibility that many metals can be separated and purified as the chelates by fractional sublimation and gas chromatography. Several groups[5-13] have demonstrated the separation of various metal chelates by gas chromatography but little or nothing has been reported on separations achieved by fractional sublimation.

The immediate objective of the present study[14] was to devise a fractional sublimation technique which would take advantage of the observed[1-4] differences in volatility among the various metal chelates, effect a separation of mixtures of metal chelates, and permit the recovery of starting materials. This is the first of several reports on these studies.

A simple but effective vacuum sublimator was developed which maintains a controlled temperature gradient along its length. Volatilized chelates are moved through the sublimator with air as a carrier. Contact of the vapor with the walls of the tube brings about a selective condensation of the metal chelates in an order of increasing volatility. Condensation (sublimation) temperatures are reported for some metal acetylacetonates and several separations and purification procedures are proposed.

EXPERIMENTAL

Apparatus

Two basic types of sublimators were tried. The first was the glass apparatus diagrammed in Fig. 1. It consists of a pyrex sublimation tube which is inserted into a series of concentric heating jackets. Each section of the heating jacket was joined to the next by ground-glass joints. By refluxing a different liquid in each section of the heating jacket, a stepped (discontinuous) temperature gradient was maintained along the sublimator tube. A typical temperature gradient obtained is shown in Fig. 2. In the original design, the internal sublimation tube was not employed but in practice it was found that recoveries were more convenient from a single tube than from the several short heating jackets in series. Separations were achieved with this equipment but the sublimator with a continuous temperature gradient along its

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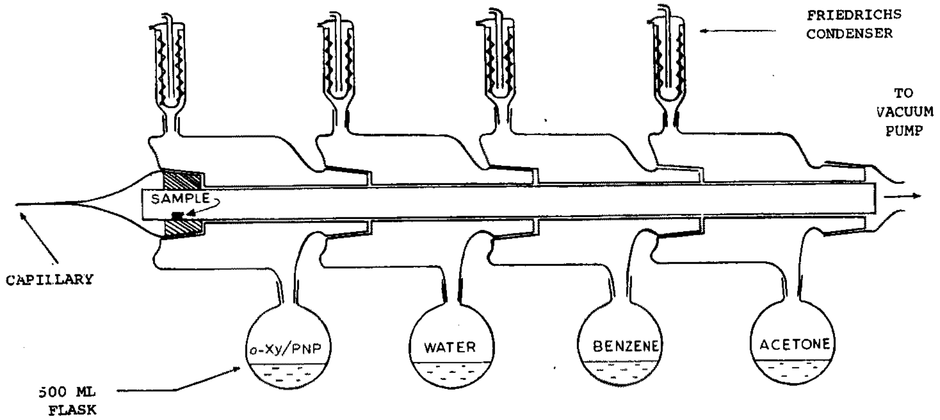

Fig. 1. Pyrex glass sublimation apparatus with discontinuous temperature gradient.

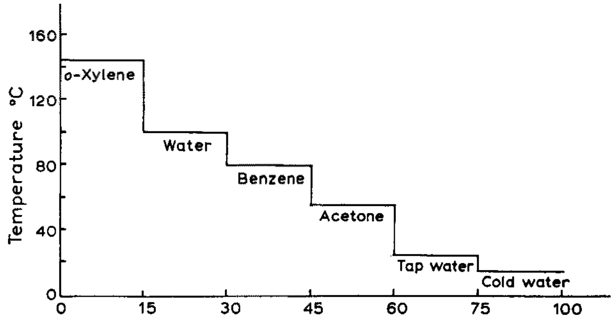

Fig. 2. Discontinuous temperature gradient along glass sublimation apparatus.

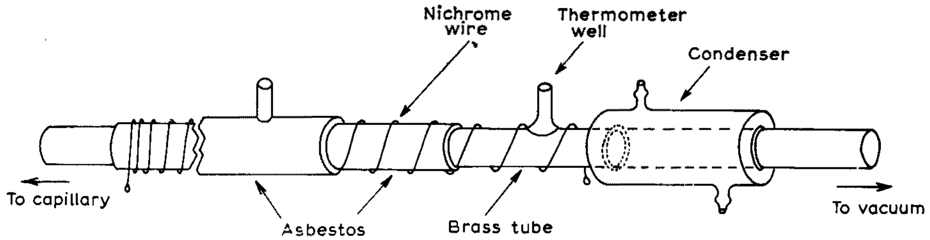

Fig. 3. Wire-wound sublimation apparatus with continuous temperature gradient.

length was far more efficient. Consequently, all data reported in this paper were collected on the sublimator possessing a continuous temperature gradient.

A schematic diagram of the sublimator devised to give a continuous temperature gradient along its length is shown in Fig. 3. Six 1″ segments of copper tubing were welded perpendicular to the axis of a 1-m brass tube (I. D. 11 mm) at 16-cm intervals to serve as thermometer wells. The tube was wrapped with one layer of asbestos paper for electrical insulation and then wrapped with No. 22 B and S nichrome wire (0.0253″ in diameter). The wire turnings were very close together (5 turns per cm) at one end of the tube but the spacing between turns increased progressively along the tube until adjacent turns were about 4 cm apart six inches from the opposite end. The nichrome wire was then covered with about 4 mm of asbestos for thermal and electrical insulation. A snug fitting 11 mm (O. D.) pyrex tube was inserted into the wire-wound brass tube. Power was supplied to the nichrome heating element from a 110-V, 60-cycle A. C. source through a powerstat (Variac). Typical temperature gradients obtained along the sublimation tube for different settings of the powerstat are given in Fig. 4. The gradients were very reproducible.

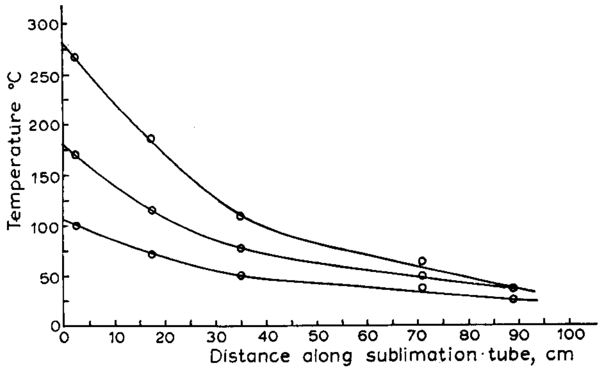

Fig. 4. Continuous temperature gradient along wire-wound sublimation apparatus.

Temperatures were checked by placing a thermometer in each thermometer well. A good contact between the thermometer bulb and the brass tube was assured by placing several drops of silicone oil in each well. Approximately the last six inches of the low temperature end of the tube was left free of windings to facilitate cooling the end with an ice water bath to ensure the complete condensation of all chelates.

Preparation of metal acetylacetonates

The following general procedure was used for the preparation of the individual metal chelates. The nitrate salt (except for beryllium as sulfate) of the metal was made up as a 5% (w/w) solution and buffered immediately before use by adding 5 g of sodium acetate for every 100 ml of solution. The buffered metal ion solution was shaken with an alcoholic solution of the acetylacetone until reaction appeared complete. The chelate was collected by filtration, washed, recrystallized from an appropriate solvent and dried. The exact procedure for the preparation and the description of the chelates is given by BERG AND TRUEMPER[1,2] and HARTLAGE[14].

Procedure

Small aluminum boats containing the samples were placed in the high temperature end of the sublimator which was then closed with a small capillary tube.

The low temperature end of the sublimator tube was connected to a continuous duty vacuum line maintained at 1 mm of mercury pressure. Pressure readings were made with a McLeod pressure gauge. Air which entered the capillary acted as a carrier gas to move the volatilized chelates through the sublimator. Samples were left in the apparatus from 1 to 2 h, after which time the pyrex tube was withdrawn from the heating jacket. Individual sublimate zones were quite obvious visually and generally sharply defined. The method of recovery involved cutting out the section of pyrex tube containing the desired component and retrieving the sublimate manually or by dissolving it in an appropriate solvent. The temperature ranges in which the individual chelates were observed to condense are reported in Table I. In most instances the high temperature end of the zone was rather sharply defined.

TABLE I

SUBLIMATION RECRYSTALLIZATION ZONES FOR VARIOUS METAL ACETYLACETONATES

I	*II*	*III*	*IV*	*V*	*VI*
Ca(II) 203–167	Mg(II) 141–120	Zr(IV) 102–77	Mn(II) 90–70	Zn(II) 38–31	Be(II) 31–15
	Cd(II) 137–117	V(III) 111–94	Fe(III) 85–66		
		Cr(III) 106–80	Co(II) 88–67		
		Rh(III) 118–96	Pd(II) 94–74		
		Ni(II) 111–88	Hg(II) 75–55		
		Pt(II) 102–80	Ga(III) 92–70		
		Cu(II) 102–82	In(III) 85–66		
		Th(IV) 116–78	Al(III) 81–60		

The chelates of iron, beryllium, aluminum, magnesium and nickel were recovered from the sublimation tube and analyzed directly for the metal content to determine the percentage recovery. In all other cases, the percentage recovery was determined from the measured loss in weight of samples during the sublimation. This latter method was used because of its simplicity and the fact that it gave results with Fe, Be, Al, Mg and Ni which were consistent with the more tedious direct analysis. Without any positive evidence that the sublimed compounds decomposed (below

TABLE II

SOME COMPLETE SEPARATIONS THAT CAN BE ACHIEVED WITH THE ACETYLACETONATES

Mg, Mn and Zn	Ca, Zr and Zn	Cd, Mn and Zn
Mg, Fe and Be	Ca, V and Be	Cd, Zr and Be
Mg, Co and Zn	Ca, Cr and Zn	Cd, Fe and Zn
Mg, Pd and Be	Ca, Rh and Be	Cd, Cr and Be
Mg, Hg and Zn	Ca, Ni and Zn	Cd, Pd and Zn
Mg, Ga and Be	Ca, Pt and Be	Cd, Ni and Be
Mg, In and Zn	Ca, Cu and Zn	Cd, Ga and Zn
Mg, Al and Be	Ca, Th and Be	Cd, Cu and Be
Mg, Zr and Zn	Ca, Mn and Zn	Cd, Co and Zn
Mg, V and Be	Ca, Fe and Be	Cd, Hg and Be
Mg, Cr and Zn	Ca, Co and Zn	Cd, In and Zn
Mg, Ni and Be	Ca, Pd and Be	Cd, Al and Be
Mg, Pt and Zn	Ca, Hg and Zn	Cd, V and Zn
Mg, Cu and Be	Ca, Ga and Be	Cd, Pt and Be

200°) or recrystallized in areas other than the defined zones, it was assumed that the latter method gave correct recovery values. Percentage recovery values are reported in Table II.

Analytical methods

In determining the metal content of the chelates, the compound was decomposed with nitric acid, the residue diluted to volume with distilled water, and an aliquot taken for analysis. Iron was determined by a modified version of the 1,10-phenanthroline method; nickel with dimethylglyoxime; beryllium with *p*-nitrobenzeneazoorcinol; aluminum with aluminon reagent; and magnesium with eriochrome black T.

DISCUSSION

The manner of presenting the data here does not do justice to the sharpness of the sublimate zones observed in the sublimation tube. The zones are sharply defined in most instances with little or no evidence of crystals lying outside the temperature range reported. The high temperature end of the zone is usually the sharper of the two. On the assumption that each metal chelate will behave independently of other chelates in the sublimation apparatus (an assumption shown to be valid in separational studies) it is apparent from the sublimation temperature zones reported in Table I that many separations are possible by this technique.

Groups of elements which should be completely resolved by the fractional sublimation of their acetylacetonates are listed in Table II.

Admittedly, many of the possible separations listed are not of any particular analytical interest and may not be realized in practice because the chelates are not all produced under identical conditions. Nevertheless, the list is submitted as a means of correlating much of the physical data collected with synthetic samples made up of pure metal chelates.

A number of the indicated separations were tried and a few were studied sufficiently to give a truly quantitative character to the efficiency of the technique.

TABLE III

PERCENTAGE RECOVERY DETERMINATION OF SOME OF THE ACETYLACETONATES WITH A TEMPERATURE GRADIENT OF 170° TO 15°

Metal	*Chelate taken (mg)*	*Metal ion taken (mg)*	*Metal ion found (mg)*	*Chelate remaining (%)*	*Recovery (%)*
Al	19.8	1.65	1.63	2.3	98.5
Be	19.6	0.85	0.86	0.0	101.0
Fe	18.4	2.92	2.80	3.8	95.8
Mg	25.9	2.62	1.78	33.0	67.7
Ni	14.0	2.81	2.58	10.0	91.8
Cd	7.8	—	—	12.7	87.3
Co	31.6	—	—	0.6	99.4
Cu	11.6	—	—	6.0	94.0
Ga	23.7	—	—	0.9	99.1
Pd	8.5	—	—	1.2	98.8
Zn	24.3	—	—	7.4	92.6

Typical of the fractional sublimation of elements whose recrystallization zones are widely separated is the separation of mixtures of magnesium, aluminum and beryllium. The analytical data for such separations are given in Table III. It is quite evident that sensitive chemical analyses substantiate the visually observed quantitativeness of the separations. No trace of metal impurity was detectable in any of the individual zones. It is to be noted also that the percentage recovery of the aluminum and beryllium was essentially complete. As might be expected, the magnesium acetylacetonate was not too stable and some decomposition in the sample boat reduced the percentage recovery. These recovery values should be compared with those observed for a number of the individual chelates reported in Table IV. With the exception of the Mg, Ca and Cd acetylacetonates, the recovery of the metal chelates ranged from 90 to 100%. These 3 exceptions are the least volatile of the chelates reported on.

Mixtures of Mg, Al and Be salts were treated with acetylacetone and the chelates collected, washed, dried, and sublimed in the apparatus. Aluminum and beryllium were recovered in pure fractions, but not quantitatively; the yields were not quantitative because of the incomplete precipitation of the chelates and not because of the incomplete sublimation of the chelates. The formation of the chelates

TABLE IV

ANALYTICAL DATA OF THE SEPARATION OF MAGNESIUM, ALUMINUM AND BERYLLIUM ACETYLACETONATES WITH A TEMPERATURE GRADIENT OF 170° TO 15°

Metal taken (mg)	*Metal found in Mg fraction (mg)*	*Metal found in Al fraction (mg)*	*Metal found in Be fraction (mg)*	*Recovery in pure form (%)*
No. I				
Mg — 0.120	0.079	0.00	0.00	66.0
Al — 0.117	0.00	0.120	0.00	102
Be — 0.045	0.00	0.00	0.046	102
No. II				
Mg — 0.229	0.150	0.00	0.00	65.5
Al — 0.200	0.00	0.196	0.00	98.0
Be — 0.093	0.00	0.00	0.089	96.0

TABLE V

ANALYTICAL DATA FOR THE SEPARATION OF NICKEL, IRON AND BERYLLIUM ACETYLACETONATES WITH A TEMPERATURE GRADIENT OF 170° TO 15°

Metal taken (mg)	*Metal found in Ni fraction (mg)*	*Metal found in Fe fraction (mg)*	*Metal found in Be fraction (mg)*	*Recovery in pure form (%)*
No. I				
Ni — 0.241	0.164	0.051	0.00	68
Fe — 0.254	0.00	0.238	0.00	—
Be — 0.070	0.00	0.00	0.069	99
No. II				
Ni — 0.120	0.100	0.013	0.00	83
Fe — 0.111	0.00	0.104	0.00	—
Be — 0.037	0.00	0.00	0.036	97

is quite pH dependent. Magnesium acetylacetonate forms only to a slight extent under the same conditions as the Al and Be chelates and does not appear as a sublimate zone. Thus, ionic mixtures of Mg, Al, and Be can be resolved by this technique (albeit Mg is lost by default) but not quantitatively.

Typical of the separations of elements whose recrystallization zones closely border or overlap each other are the separations of mixtures of nickel, iron and beryllium and mixtures of copper and iron. The analytical data for the separation of mixtures of Ni, Fe and Be are given in Table V and for Cu and Fe in Table VI.

TABLE VI

ANALYTICAL DATA FOR THE SEPARATION OF COPPER AND IRON ACETYLACETONATES WITH A TEMPERATURE GRADIENT OF 170° TO 15°

Metal taken (mg)	*Metal found in Cu fraction (mg)*	*Metal found in Fe fraction (mg)*	*Recovery in pure form (%)*
No. I			
Cu — 0.342	0.238	0.085	70
Fe — 0.222	0.00	0.210	—
No. II[a]			
Cu — 0.320	0.225	0.073	70
Fe — 0.206	0.00	0.188	—

[a] Sample II was sublimed in a tube packed with 3 mm glass helices.

Although the sublimation zones of Ni and Fe, and Cu and Fe overlap each other it is possible to recover up to 83% of the Ni and 70% of the copper in pure form. The beryllium is of course recovered quantitatively in pure form. A relatively high percentage of the iron is recoverable in pure form also but this observation was not verified with these samples. The intense colors of the Fe, Cu and Ni chelates give an excellent visual indication of the extent to which zones overlap.

Mixtures of Ni, Cu, Fe and Be have been effected with only a slight overlapping of the Ni and Cu, and the Cu and Fe zones. No analyses were performed on these zones but it was estimated visually that at least 75% of each chelate was recoverable in pure form. The recovery of beryllium would be quantitative.

It should be possible to separate quantitatively mixtures of zinc, cadmium and mercury. The sublimation zones are quite distinct and separate for each. An added inducement here comes from the fact that the 3 metals form the acetylacetonates under similar conditions. Preliminary studies on this group have indicated that the mercury behaves differently in mixtures of the 3 elements than when alone but excellent separations of Zn and Cd have been effected.

An interesting consequence of these sublimation studies is the observation that some of the platinum group metals form volatile acetylacetonates which are recoverable in high yields. There appears little chance to effect separations within the group of platinum metals but it should be possible to separate the platinum group metals from the base metals used in their metallurgy. Such a separation was observed in this study but not recognized at the time of occurrence. A sample of presumably pure $RhCl_3$ was dissolved, converted to the acetylacetonate, and the chelate sublimed in the apparatus. Immediately adjacent to the high temperature end of the rhodium sublimation zone was a very distinct white crystalline zone about 1 cm long. Subsequent investigations showed this white zone to be magnesium acetylacetonate. Undoubtedly, magnesium had been used as the base metal for the reduction of the iridium and rhodium in their metallurgy and remained as a contaminant; Mg, Zn, and Pb are familiar contaminants in the commercially available Rh and Ir. This fractional sublimation scheme offers a convenient means of freeing the platinum metals from these base metals.

The very nature of this technique suggests several refinements which conceivably might enhance its resolving power. The most obvious variables are the sample size, column packing, temperature gradients, and the geometry of the sublimation tube. Thorough studies on the effect of these variables on separation efficiency have not been made to date but some tentative conclusions can be drawn. With an 11-mm (O.D.) sublimation tube, the maximum sample size which will allow for good separations of metals with bordering sublimation zones is from 10 to 50 mg. For mixtures of this type a smaller sample should yield a better separation. This is evident for the separation of nickel and iron reported in Table V. Larger samples may be used without a decrease in efficiency where the sublimation zones of the metals to be resolved differ by many degrees or where only traces of other elements need be purged in a purification.

Several separations were attempted with columns packed with 3-mm glass helices but the comparison of results obtained with unpacked tubes did not warrant the continued use of a packing.

Certainly in some instances, variations in tube geometry and temperature gradients will enhance the separation efficiency.

In summary it might be said that the fractional sublimation technique described here provides a very simple and effective method of resolving many mixtures of metal acetylacetonates. In many respects, the separations compare favorably with the separations achieved by gas chromatography, yet samples large enough for preparative purposes may be employed.

ACKNOWLEDGEMENTS

F. R. H. is indebted to Louisiana State University for the graduate research assistantship which supported this study. The authors are indebted to FRED DOWLING for the design of the all-glass sublimator.

SUMMARY

A simple fractional sublimator is described which possesses a continuous temperature gradient along its length. Samples are placed in the high temperature end of the tube and volatilized at 1-mm pressure. The gases are moved through the tube with air as a carrier. The metal chelates recrystallize on the walls of the tube in discrete and reproducible temperature zones. Characteristic recrystallization zones are reported for 21 metal acetylacetonates. The chelates can be grouped according to zone temperatures into 6 fairly distinct groups over the range 15 to 200°, which makes many separations possible. Separations of mixtures of Mg, Al and Be; Ni, Fe and Be;

and, Cu and Fe were studied quantitatively. The separations achieved compared favorably with those reported by gas chromatography.

The method offers real promise for the purification of a number of metals but appears especially good as a method for beryllium and certain platinum group metals.

RÉSUMÉ

Les auteurs ont examiné la sublimation fractionnée de divers acétylacétonates métalliques. On décrit l'appareil; l'échantillon, placé à l'extrémité 'haute température' du tube, est volatilisé à une pression de 1 mm. Les chélates métalliques recristallisent sur les parois du tube, en zones distinctes et reproductibles. Les zones caractéristiques de recristallisation sont données pour 21 acétylacétonates métalliques; de nombreuses séparations sont possibles, pouvant se comparer avantageusement avec celles obtenues par chromatographie gazeuse. Ce procédé peut être utilisé également pour la purification d'un certain nombre de métaux, en particulier le béryllium et des métaux du groupe du platine.

ZUSAMMENFASSUNG

Es wird eine einfache Apparatur zur fraktionierten Sublimation von Metallchelaten beschrieben, die einen kontinuierlichen Temperaturgradienten auf der gesamten Länge einer Röhre besitzt. Die Proben werden an dem Ende der Röhre, das eine hohe Temperatur besitzt, bei 1 mm Druck verdampft, und die Gase durch die Röhre mit Luft als Träger bewegt. Die Metallchelate rekristallisieren auf den Wänden der Röhre in bestimmten und reproduzierbaren Temperaturzonen. Es werden charakteristische Rekristallisationszonen für 21 Metallacetylacetonate angegeben. Die Chelate können je nach den verschiedenen Temperaturzonen über einen Bereich von 15 bis 200° in 6 Gruppen zusammengefast werden, so dass zahlreiche Trennungen möglich sind. Trennungen von Mischungen des Mg, Al und Be; Mi, Fe und Be; und Cu und Fe wurden quantitativ untersucht. Die Trennungen sind günstig gegenüber denen, die mit der Gaschromatographie erzielt wurden. Diese Methode bietet Vorteile für die Reinigung einer Zahl von Metallen und erscheint besonders geeignet für die Abtrennung von Beryllium und einigen Metallen der Platingruppe.

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STUDIES ON RARE EARTH 1,3-DIKETONATES

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Most methods for the preparation of the acetylacetonates of rare earths[1] involve the addition of sodium or ammonium acetylacetonates to a dilute solution of the rare earth nitrate, but yields are generally poor. The preparation of acetylacetonates in the present investigation was based on the method of MOELLER AND FRINCH[2]. The procedure for the preparation of benzoylacetonates, dibenzoylmethides, 2-thenoyltrifluoroacetonates and dithenoylmethides was basically that of SACCONI AND ERCOLI[3], except the mixtures were adjusted to the optimum pH given by STITES AND MCCARTY[1] for precipitation of each rare earth ion.

EXPERIMENTAL

Equipment

Ultraviolet spectra were measured in a Beckman DU spectrophotometer, with a hydrogen lamp as source. For measurements in the visible region, a tungsten lamp was used. Infrared spectra were recorded in the range 2–15 μ with a Perkin-Elmer double-beam automatic recording spectrophotometer with sodium chloride optics. The compounds were examined as solids in Nujol mulls.

Materials

Rare earth oxides. Spectrographically pure oxides (99% pure) of the individual rare earth elements were obtained from Johnson, Matthey, Ltd., London.

Solvents. The organic solvents employed were of reagent quality and were dried before use.

Diketones. Acetylacetone[4], benzoylacetone[4] and dibenzoylmethane[5] were prepared by published procedures. 2-Thenoyltrifluoroacetone (L. Light, London) was purified by dissolving in ether and shaking with a saturated solution of copper acetate; the green copper derivative was treated with dilute sulphuric acid and the ethereal layer was evaporated to dryness (residue: m.p. 75–76°). A sample of dithenoylmethane (m.p. 100°) was obtained from the Department of Chemistry, Penn. State University, U.S.A. and was used without further purification.

Preparation of chelates

Rare earth acetylacetonates. The oxide sample (2 g) was dissolved in A.R.

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hydrochloric acid and, after concentration by heating, the solution was added to a slight excess of acetylacetone in 100 ml of 1:1 water–dioxane. The solution was vigorously stirred and the pH adjusted by the dropwise addition of ammonia solution just short of precipitation of the rare earth hydroxide. The crystalline product was filtered, washed with ethanol and dried over magnesium perchlorate in a vacuum desiccator.

Rare earth benzoylacetonates and dibenzoylmethide chelates. The rare earth oxide (2 g) was dissolved in 10 ml of A.R. nitric acid and the solution was carefully evaporated to dryness on a water bath, to remove the acid. The residue was dissolved in 15 ml of absolute ethanol to which 3 g of the ligand in 40 ml of alcohol were added and the pH adjusted to the optimum value by the addition of alcoholic ammonia. The abundant precipitate formed was filtered, washed with a little alcohol, dissolved in benzene and filtered from any insoluble residue. The solution was allowed to evaporate at room temperature and the compound was vacuum-dried over concentrated sulphuric acid.

Rare earth 2-thenoyltrifluoroacetonates and dithenoylmethide chelates. The method adopted for benzoylacetonates and dibenzoylmethides was extended for 2-thenoyltrifluoroacetonates and dithenoylmethide chelates. The melting points and colours of all these chelates are shown in Table I. It was shown (a weighed amount of the dried chelate was ignited in a platinum crucible and the residual oxide weighed) that the metal to ligand ratio was 1:3 except in the case of cerium (1:4). Elemental analyses were carried out for the 5 different chelates of Gd, Er and Yb. The acetylacetonates and benzoylacetonates gave results within the accepted limits of accuracy; with dibenzoylmethides, the carbon values were generally 1% low and the metal values 1% high. The 2-thenoyltrifluoroacetonates gave accurate results for C, H, S, F and metal, except for the Er and Yb chelates, where the carbon values were *ca.* 1% low. With the dithenoylmethides practically all the values found for C, H, S and metal were 0.5–1% low.

ULTRAVIOLET MEASUREMENTS

The rare earth 1,3-diketonates in the ultraviolet region of 200–360 mμ are subject to several limitations: (*1*) the sparingly soluble nature of the complexes in solvents transparent to this region and (*2*) the high absorption of the reagent compared to that of metal ions. Investigations were therefore confined to methanol, ethanol, *n*-hexane and cyclohexane. The absorptivity of the organic ligands masks any splitting or structure developed by metal ions and hence one can only look for wavelength shifts in the absorption bands associated with the ligands.

Acetylacetone

In methanol this reagent absorbs between 220 and 310 mμ with an intense peak between 265 and 275 mμ and a molar extinction coefficient $\varepsilon = 8{,}130$ (*cf.* MOELLER AND FRINCH[2]; $\varepsilon = 11{,}080$ in chloroform). From Table II it is clear that all the spectra are solvent-dependent. In ethanol the wavelength at the band maximum remains the same as in methanol but the intensity decreases appreciably. In *n*-hexane and cyclohexane there are slight blue shifts in the band maximum relative to methanol as well as a decrease in intensity. The spectra of the corresponding rare earth chelates indicate a general red shift and an increase in ε relative to the reagent in the solvents employed.

TABLE I

PROPERTIES OF CHELATES

Metal	pH of pptn.	Acetylacetonates			Benzoylacetonates			Dibenzoylmethides			2-TTA		Dithenoylmethides	
		M.p.[a]	M.p.[b]	Color[c]	M.p.[a]	M.p.[b]	Color	M.p.[b]	M.p.[b]	Color	M.p.[b]	Color	M.p.[b]	Color
La	6.5	—	—	—	108–9	120	y	142–5	142	o	135	b	—	—
Ce	5.6	—	—	—	187–8	185	b	192–3	192	b	181	b	—	—
Pr	6.5	144–5	144–5	g	106–8	108	gy	149–51	210–15	y	164	b	230	gy
Nd	6.5	144–5	144–5	p	106–8	107	p	147–50	215–7	p	181–2	p	200	gy
Sm	6.5	144–5	144–5	y	103–5	104	s	148–9	180–2	gy	148	s	165	y
Eu	6.5	—	—	—	—	155	y	—	215	y	180	p	171	y
Gd	6.5	—	182–4	sy	100–1	100	p	214–6	216	y	122	gr	222	y
Tb	6.4	—	—	—	—	140	gy	—	202	b	115	p	—	—
Dy	5.8	—	144–5	w	—	148–150	sy	—	215–8	y	193	y	212	y
Ho	6.5	—	—	—	—	144	sy	—	235	y	135	b	—	—
Er	6.5	142–4	161	p	—	142	y	—	225	p	125	p	210	y
Tm	6.4	—	—	—	—	118	r	—	178	y	115	b	—	—
Yb	6.2	—	165	s	—	125	r	—	205–8	b	145	y	216	y

[a] Reported[2,3].
[b] Found.
[c] g = green; p = pink; s = straw; w = white; y = yellow; b = brown; r = red; o = orange; gr = grey.

TABLE II

ABSORPTION BANDS OF RARE-EARTH ACETYLACETONATES

Substance	*Methanol*		*Ethanol*		*n-Hexane*		*Cyclohexane*	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Acetylacetone	275	8,130	275	501	270	1,000	270	159
Gd(AA)$_3$	290	25,120	273	31,620	275	5,012	273	3,981
Dy(AA)$_3$	286	36,920	—	—	—	—	—	—
Er(AA)$_3$	290	39,810	280	25,120	280	19,950	280	25,120
Yb(AA)$_3$	290	31,620	275	31,620	275	15,850	280	19,950

Benzoylacetone

This unsymmetrical 1,3-diketone has been studied by MORTON *et al.*[6]. The absorption spectrum in methanol was shown to exhibit peaks at 307 mμ and 246.5 mμ. MORTON *et al.* suggested that there is a keto–enol equilibrium in methanol with 90% of the compound existing in the enolic form; in order to account for the difference in ε values at 307 mμ and 247 mμ, a ketonic form with maximum absorption at 247 mμ and two enolic forms differentiated by the separation of the hydroxyl and phenyl group, both with a maximum at 307 but only one absorbing at 247 mμ were postulated. The spectral data for these two bands, in the various solvents used, are reported in Table III.

TABLE III

ABSORPTION BANDS OF RARE-EARTH BENZOYLACETONATES

Substance	*Methanol*		*Ethanol*		*n-Hexane*		*Cyclohexane*	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Benzoylacetone	250	5,012	245	3,612	250	5,012	250	7,943
	310	12,590	305	10,000	305	10,000	305	19,950
La(BZA)$_3$	245	15,850	250	7,943	240	12,950	240	19,950
	320	25,120	315	12,590	305	15,850	315	31,620
Ce(BZA)$_4$	240	25,120	240	12,590	240	12,950	240	15,850
	330	50,120	330	25,120	315	15,850	315	31,620
Pr(BZA)$_3$	240	25,030	—	—	—	—	—	—
	330	15,880	—	—	—	—	—	—
Nd(BZA)$_3$	247	12,980	—	—	—	—	—	—
	310	20,940	—	—	—	—	—	—
Sm(BZA)$_3$	245	13,680	—	—	—	—	—	—
	330	25,420	—	—	—	—	—	—
Eu(BZA)$_3$	245	7,943	245	10,000	245	1,000	245	2,512
	320	12,590	315	15,850	305	5,012	315	5,012
Gd(BZA)$_3$	240	25,120	250	15,850	250	15,850	245	10,000
	325	50,120	315	39,810	305	39,810	310	10,000
Tb(BZA)$_3$	240	19,950	240	5,012	245	6,310	240	3,162
	325	39,810	330	7,943	315	12,590	315	5,012
Dy(BZA)$_3$	240	45,800	—					
	325	70,690	—					
Ho(BZA)$_3$	245	7,943	245	7,943	245	5,012	245	3,162
	320	19,950	315	12,590	305	15,850	305	6,310
Er(BZA)$_3$	240	31,620	240	3,162	240	5,012	240	10,000
	325	63,100	330	6,310	310	19,950	315	19,950
Tm(BZA)$_3$	245	6,310	250	6,310	250	7,943	240	2,512
	320	15,850	310	15,850	305	19,950	310	6,310
Yb(BZA)$_3$	240	15,270	—					
	320	23,120	—					

The solvent clearly affects the extinction value with only small band shifting.

The absorption of the praseodymium chelate follows a rather peculiar course. Between 220 mμ and 250 mμ a broad shoulder appears as if it were a composite picture of two over-lapping absorptions. This probably arises from band shifting upon chelation; the praseodymium ion has no absorption in this region of the spectrum.

In each of the other chelates investigated two band maxima appear with some slight shifting. All the bands are broad.

TABLE IV

ABSORPTION BANDS OF RARE-EARTH DIBENZOYLMETHIDES

Substance	*Methanol*		*Ethanol*		*n-Hexane*		*Cyclohexane*	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Dibenzoylmethane	250	7,925	265	12,590	250	19,950	250	5,012
	342	19,200	355	15,850	355	31,620	335	12,590
La(DBM)$_3$	250	10,000	260	50,120	250	31,620	250	15,850
	350	19,950	350	63,100	335	79,430	345	31,620
Ce(DBM)$_4$	250	39,810	255	63,100	250	25,120	250	15,850
	345	63,100	350	100,000	340	63,100	340	25,120
Pr(DBM)$_3$	251	31,660	—	—				
	290	12,090	—	—				
	348	51,290	—	—				
Nd(DBM)$_3$	250	29,550	—	—				
	350	48,970	—	—				
Sm(DBM)$_3$	252	38,180	—	—				
	349	62,650	—	—				
Eu(DBM)$_3$	250	79,430	265	39,810	250	25,120	250	15,850
	355	125,900	350	63,100	340	63,100	340	39,810
Gd(DBM)$_3$	254	63,100	260	19,950	250	19,950	250	31,620
	353	100,000	350	31,620	340	63,100	340	63,100
Tb(DBM)$_3$	250	50,120	260	31,620	250	12,590	250	39,810
	350	100,000	350	50,120	340	31,620	340	79,430
Dy(DBM)$_3$	250	13,390	—	—				
	350	21,930	—	—				
Ho(DBM)$_3$	255	15,850	260	25,120	250	25,120	250	39,810
	350	31,620	350	39,810	340	79,430	340	100,000
Er(DBM)$_3$	250	7,943	260	25,120	250	7,943	250	15,850
	350	15,850	350	50,120	340	19,950	340	31,620
Tm(DBM)$_3$	252	63,100	255	25,120	250	25,120	250	25,120
	350	100,000	350	50,120	340	63,100	340	63,100
Yb(DBM)$_3$	255	34,260						
	349	54,110						

Dibenzoylmethane

The spectrum of this 1,3-diketone has also two absorption band maxima (Table IV). Because of symmetry there is only one enolic structure associated with the diketone.

In methanol the praseodymium chelate exhibits a third intermediate band of low intensity at 290 mμ; $\varepsilon = 12{,}090$. With the exception of the dysprosium chelate, which presents rather diffuse absorption bands, all of the other chelates exhibit strong bands with ratio of ε_{max} values equal approximately to a factor of 2.

2-Thenoyltrifluoroacetone

The spectrum of this diketone shows 3 well-defined bands in methanol, the band at 285 mμ being rather diffuse. With the other solvents only two bands are obtained. The band at 285 mμ most probably merged with the one at 260 mμ. The spectral data are summarised in Table V.

The neodymium chelate shows an additional band of low intensity, wide and unsymmetrical at 240 mμ. Other elements show two bands.

TABLE V

ABSORPTION BANDS OF RARE-EARTH THENOYLTRIFLUOROACETONATES

Substance	*Methanol*		*Ethanol*		*n-Hexane*		*Cyclohexane*	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
2-Thenoyltri-fluoroacetone	260	7,239	288	7,943	265	6,310	270	6,310
	285	5,416	—	—				
	338	7,546	340	19,950	345	5,012	345	7,943
La(TTA)$_3$	270	5,012	299	2,512	270	15,850	270	10,000
	344	25,120	345	12,590	340	39,810	344	12,590
Ce(TTA)$_4$	265	12,590	270	10,000	280	10,000	275	5,012
	340	39,810	340	31,620	340	19,950	340	10,000
Pr(TTA)$_3$	264	12,590	275	12,590	280	10,000	275	3,162
	339	25,120	339	31,620	340	19,950	340	7,943
Nd(TTA)$_3$	240	8,215						
	270	17,380						
	340	50,930						
Sm(TTA)$_3$	266	26,730						
	344	68,050						
Eu(TTA)$_3$	268	19,950	270	10,000	270	10,000	275	12,590
	340	50,120	340	50,120	340	25,120	340	25,120
Gd(TTA)$_3$	268	25,120	270	10,000	275	7,943	275	15,850
	341	79,430	340	31,620	340	39,810	340	31,620
Tb(TTA)$_3$	265	15,850	270	12,590	275	19,950	275	15,850
	340	63,100	340	38,810	340	39,810	340	31,620
Dy(TTA)$_3$	269	18,220	270	19,950	275	7,943	275	12,590
	344	51,770	340	50,120	340	12,590	340	19,950
Ho(TTA)$_3$	265	19,950	270	19,950	275	7,943	275	12,590
	340	63,100	340	50,120	340	12,590	340	19,950
Er(TTA)$_3$	265	15,850	280	7,943	275	15,850	275	19,950
	340	50,120	340	25,120	340	39,810	340	50,120
Tm(TTA)$_3$	265	15,850	275	31,620	275	10,000	275	19,950
	340	50,120	340	79,430	340	19,950	340	50,120
Yb(TTA)$_3$	265	17,490						
	342	62,790						

Dithenoylmethane

The absorption spectrum of this compound in the solvents employed shows two absorption bands. There is little band maxima shift and the extinction coefficients show some variation with solvent. The spectral results are summarised in Table VI.

TABLE VI

ABSORPTION BANDS OF RARE-EARTH DITHENOYLMETHIDES

Substance	*Methanol*		*Ethanol*		*n-Hexane*		*Cyclohexane*	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Dithenoylmethane	265	12,590	275	6,310	270	7,943	270	6,310
	375	25,120	375	12,590	365	19,950	370	15,850
$Pr(DTM)_3$	270	15,850	270	25,120	270	5,012	270	1,585
	380	31,620	380	63,100	370	7,943	370	3,162
$Nd(DTM)_3$	270	31,620	270	25,120	270	1,995	270	2,512
	385	79,430	380	63,100	365	6,310	365	5,012
$Sm(DTM)_3$	265	15,850	270	19,950	270	7,943	270	3,981
	380	31,620	380	39,810	370	15,850	370	7,943
$Eu(DTM)_3$	270	25,120	270	15,850	270	6,310	270	5,012
	380	50,120	380	31,620	370	15,850	370	12,590
$Gd(DTM)_3$	270	15,850	270	19,950	270	10,000	270	6,310
	380	31,620	380	39,810	370	15,850	370	10,000
$Dy(DTM)_3$	275	3,162	270	15,850	270	3,162	270	1,585
	380	10,000	380	39,810	370	6,310	370	3,162
$Er(DTM)_3$	270	39,810	270	19,950	275	1,995	270	5,012
	385	100,000	380	63,100	370	3,981	370	10,000
$Yb(DTM)_3$	270	31,620	270	19,950	265	2,512	270	2,512
	380	63,100	380	50,120	370	6,310	370	5,012

MEASUREMENTS IN THE VISIBLE REGION

Many investigations have been made on the absorption spectra of rare earth complexes in order to evaluate the relation between the structure and splitting pattern. Hölleck and Eckhardt[7] observed splitting of the 575-mμ neodymium band on complexation. Splitting of the 523-mμ band of erbium was also noticed when it was complexed with various ligands.

Some valuable observations were made on the complexes with EDTA by Moeller[8]. Absorption spectra of neodymium chloride solution containing varying quantities of EDTA were measured over the range 250–1000 mμ. In the range 510–1000 mμ every neodymium band was split into two or more components indicating interactions between neodymium and EDTA ion in solution. These studies on the neodymium complex with EDTA were extended to other rare earths by Vickery[9]. Hölleck[10] observed splitting in the region of 400–800 mμ in neodymium, praseodymium and samarium complexes with citric acid, sulphosalicylic acid, EDTA, and ethyleneglycol (2-amino ethylether) tetraacetic acid.

The chelation of elements 95–100 with thenoyltrifluoroacetone was also studied[11]. A study of the spectra of complexes in non-aqueous solvents[12] revealed that the enhanced stability of the chelate is reflected in the spectral alterations. Moeller and Frinch[2] studied the absorption spectra of some rare earth elements with acetylacetone. Since 1,3-diketone chelates of the tripositive rare earth ions are very stable, the present work was carried out to study the influence of the chelate type on the spectral characteristics.

In the following discussion of the spectra of the various rare earth complexes, a comparison of the spectra of the metal nitrate (in aqueous solution) and of the chelates formed with benzoylacetone, dibenzoylmethane, 2-thenoylfluoroacetone and dithenoylmethane is made. In general a splitting of the band or bands was observed on chelate formation.

Praseodymium

In the benzoylacetonate the 444-mμ band of the praseodymium nitrate in water shows a minute bathochromic shift to 448 mμ or 450 mμ. At this point the absorption due to the ligand is negligible and no intensification appears to result from chelation in acetone, methanol or benzene media. This may also be said of the bands at 480 mμ and 590 mμ.

In the dibenzoylmethide, again a minute bathochromic shift appears. In methanol all 3 bands become more intense, while no such effects are perceivable in acetone. Strangely, the bands at 590 mμ and 444 mμ are absent in benzene.

The praseodymium 2-thenoyltrifluoroacetonate shows no selective absorption in the visible region.

In the dithenoylmethide, the bands at 444 mμ and 480 mμ could not be located in the solvents employed. A band was located at 520 mμ in all the solvents. The band at 590 mμ might thus have shifted.

MOELLER AND FRINCH[2] located all the 3 bands in benzene solutions of the acetylacetonates.

The molar extinction coefficients for all the reagents and chelates were of the order of 1–40.

Neodymium

This element is the most interesting of the series. The benzoylacetonate shows at least 4 bands in all the solvents. The metal nitrate shows prominent bands at 745, 576, 522 mμ. These are shifted in the benzoylacetonate to 750, 584(586), 572, 530 mμ and are the most highly intensified.

The dibenzoylmethide exhibits similar characteristics in methanol and in addition the feeble neodymium band at 512 mμ appears at 514 mμ with enhanced intensity. In acetone and benzene there is no splitting and in the latter the 512 mμ band is shifted to 518 mμ.

In the 2-thenoyltrifluoroacetonate, the most notable feature is the appearance of a fairly intense peak at 540 mμ in methanol.

In the dithenoylmethide chelate in the solvents employed, the absorption bands at 520 mμ and 576 mμ are split. Strangely, the absorption peak at 745 mμ is absent in all the solvents investigated. The results found are shown in Table VII.

Samarium

The trivalent ion has only one peak at 402 mμ. At this wavelength all the diketonates have measurable absorptions in all the solvents. No selective absorption was noticeable from 400 to 600 mμ with any one of the reagents, but the chelates show intense absorption. In the case of the acetylacetonates the band at 402 mμ was resolved into two peaks, one at 402 and the other at 404 mμ[2].

Europium

None of the chelates shows selective absorption at 395 mμ, where the element itself has a sharp absorption. Most probably this absorption band was masked by the reagent.

TABLE VII

ABSORPTION BANDS OF NEODYMIUM CHELATES

Nitrate–water		*Acetone*		*Methanol*		*Benzene*		*Ethanol*	
λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
Neodymium				*Neodymium benzoylacetonate*					
521.5	7.9	530	10.1	530	4.2	530	5.4	—	—
576	12.6	576	26.7	572	12.4	576	17.3	—	—
745	12.6	584	32.4	584	19.9	586	21.8	—	—
796	15.8	750	6.3	750	3.7	750	3.8	—	—
		810	9.4	810	3.8	810	6.3	—	—
				Neodymium dibenzoylmethane chelate					
				514	16.8	518	10.0	—	—
		530	17.2	520	17.6	530	10.9	—	—
		588	42.9	530	20.8	590	34.5	—	—
		755	6.3	575	35.8	755	6.4	—	—
		820	6.0	586	52.9	810	7.9	—	—
				740	9.1				
				810	10.0				
				Neodymium 2-thenoyltrifluoroacetonate					
		522	21.8	520	31.1	524	15.2	—	—
		575	47.7	540	26.6	584	41.0	—	—
		740	14.3	576	46.5	745	10.0	—	—
		790	27.6	735	17.7	810	12.0		
				795	17.7			—	—
				Neodymium dithenoylmethane chelate					
				520	100.0	520	39.8	520	31.6
				525	100.0	525	39.8	525	31.6
				576	50.1	576	31.6	576	25.1
				590	79.4	590	50.1	590	39.8
				790	50.1	790	15.8	790	25.2

Gadolinium

The trivalent ion has no selective absorption in the visible region and no selective absorption could be located in any chelates.

Terbium

The trivalent ion has an absorption band at 487 mμ, but no band could be located in the chelates investigated.

Dysprosium

The trivalent ion has a strong absorption at 908 mμ. In the benzoylacetonate this is shifted to 890 mμ in methanol, 900 mμ in acetone and 910 mμ in benzene. In addition a band at 785 mμ of very low intensity is present in acetone solution.

The dibenzoylmethide is insoluble in methanol, but in acetone and benzene gives a band of medium intensity at 900 mμ (ε 6.8) and 920 mμ (ε 5.3) respectively. In the 2-thenoyltrifluoroacetonate peaks of low intensity appear at 900 mμ in methanol and acetone, and at 910 mμ in benzene. Strangely, the absorption band at 908 mμ for dysprosium in the dithenoylmethide could not be located in any solvent. In all these tests the molar extinction value lay in the range 0.8–6.8.

Holmium

The trivalent ion has absorption bands at 415, 450, 538, and 642 mμ of medium intensity ($\varepsilon \sim 10$). In the benzoylacetonate the band at 450 mμ was located with enhanced intensity (ε 316.2) but no other bands were found in methanol, ethanol or benzene.

In the dibenzoylmethide the band at 450 mμ could be located with enhanced intensity (ε 158.5) in methanol, ethanol, and benzene.

In the 2-thenoyltrifluoroacetonate the band at 450 mμ appeared in all three solvents, probably shifted to 460 mμ in ethanol. The molar extinction coefficient increased from 63.1 in methanol to 251.2 in benzene. The band at 538 mμ was located at 535 mμ in methanol and benzene.

Holmium dithenoylmethide chelate was not investigated.

Erbium

The trivalent ion has absorption at 379, 450, 487, 523, and 653 mμ of medium intensity. In the erbium acetylacetonate all the bands appear in methanol, ethanol and benzene, except the band at 653 mμ.

In the other chelates investigated (benzoylacetonate, dibenzoylmethide, and 2-thenoyltrifluoroacetonate) only two bands appear, one at 487 mμ and the other at 523 mμ, in all the solvents investigated, with slight intensification. With the dibenzoylmethide the band at 653 mμ appears only in methanol. The extinction coefficients were in the range 13–80, except for the dibenzoylmethide in methanol (ε 100.0).

In the dithenoylmethane chelate the absorption maximum at 523 mμ appears at 520 mμ with enhanced intensity (ε 158.5 in methanol and 199.5 in ethanol or benzene). Another maximum at 700 mμ was observed. Most probably the band at 653 mμ shifted to 700 mμ.

Thulium

Thulium has two absorption bands, one at 640 mμ and the other at 780 mμ of medium intensity (ε 2.0 and 3.2 respectively).

In the chelates investigated (benzoylacetonate, dibenzoylmethide and 2-thenoyltrifluoroacetonate) the band at 640 mμ was present with slight intensification (ε 20–50) in ethanol, methanol and benzene, and a slight bathochromic shift. An additional band at 950 mμ was observed in the benzoylacetonate and 2-thenoyltrifluoroacetonate.

The dithenoylmethide chelate was not prepared.

Ytterbium

Ytterbium(III) has only one absorption maximum at 980 mμ of medium intensity (ε 4.0). In the acetylacetonate, benzoylacetonate, dibenzoylmethide and 2-thenoyltrifluoroacetonate the band appeared with a slight shift without much change in intensity, in acetone, methanol, ethanol and benzene. In the dithenoylmethide no selective absorption was noticed.

INFRARED MEASUREMENTS

The infrared absorption bands arising from the C=O stretching have been extensively investigated and much data have been collected about the factors which influence their frequency and intensity. Partial enolization in simple saturated ketones is expected to cause a fall in the C=O band intensity and the appearance of O–H and C=O stretching bands. A secondary carbonyl might appear because of hydrogen bonding between ketonic and enolic species. In previous investigations[13], the C=O frequency of the diketones in the range 1770–1660 cm^{-1} was thought to arise from the presence of at least 3 molecular species.

The infrared absorption of metal acetylacetonates was studied by LECOMTE[14] and MORGAN[15]. A strong absorption band was observed between 1562 cm^{-1} and 1550 cm^{-1} in a series of 11 acetylacetonates. This band was attributed to the carbonyl group weakened by resonance between C—O—M and C=O . . . M. In all the chelates there was a second band near 1515 cm^{-1} which was attributed to the C=C bond. These findings were confirmed by BELLAMY AND BRANCH[16], who investigated various metal chelates with different diketones. The observed frequencies fell in the ranges 1608–1525 cm^{-1} and 1390–1309 cm^{-1}. A displacement of the carbonyl absorption was observed by LECOMTE, in which the 1600 cm^{-1} band was replaced by bands at 1560 and 1515 cm^{-1}, attributed to the carbonyl band and C=C absorption respectively.

Attempts were made by BELLAMY AND BRANCH[16] to relate the position of the carbonyl band with the stability of the chelates, but no definite relationship was actually established.

Investigations on the infrared spectra of chelates of other 1,3-diketones than

TABLE VIII

INFRARED ABSORPTION BANDS OF Pr, Nd, Sm, Dy, Er ACETYLACETONATES

Acetylacetone[a]	*Pr chelate*	*Nd chelate*	*Sm chelate*	*Dy chelate*	*Er chelate*	*Assignment*
	3400–3300w	3400–3200mb	3300w		3460w	OH stretch
2950w	2320w	2350w	2340w	2350w	2995w	O—H group
1740ms						Free carbonyl
1720ms						Free carbonyl
1667sh						
1650–1610bs	1610ms	1620–1590m	1610ms	1610ms	1600s	Enol chelate
	1515ms	1515ms	1515bm	1515ms	1575s	C=C link
					1510s	
1413–1410bm					1425w	$-CH_3$ (?)
1360ms	1370sh			1370sh		$C-CH_3$ (?)
1308sm	1310w		1310w	1360sh	1360s	
					1345w	
1250sm	1230wb	1260w	1220w	1260ms	1250s	=C—O
1170ms	1160wb		1160 (?)		1170mw	C=O
1156mb						
	1080–1070wb	1070wb	1075wb			
		1019sm	1019sw			
1000mb	1020–1010w			1020–1010wb	1015s	
956mb						
915ss	919w	919sm	920w	918wb	920s	
857 (?)	855w	855ws	855ws	855ws	800w	
		782w	770m	768sw		

[a] Spectrum of pure liquid.
[b] w = weak; bm = broad medium; ms = sharp medium; s = strong; sh = shoulder; wb = weak broad; sw = sharp weak; ss = strong sharp; mw = medium weak; b = broad.

acetylacetone are scanty. Experimental studies have been reported for copper chelates of thenoyltrifluoroacetone, benzoylacetone[16], dibenzoylmethane[17], trifluoroacetylacetone and hexafluoroacetylacetone[18].

A few studies have been made on the infrared spectra of unchelated 1,3-diketones including acetylacetone, dibenzoylmethane[19] and several fluorinated 1,3-diketones.

Exact information on the origin of bands of metal coordinated compounds is relatively meagre and the assignments given are only tentative. The data obtained in the present work are discussed below.

Acetylacetonates

The free carbonyl band observed at 1720 cm^{-1} in the pure liquid was absent in all the chelates; this agrees with earlier work[14–16,20].

The enol chelate band at 1615 cm^{-1} possibly was present in all the chelates at 1610–1620 cm^{-1}. Further, a new band of moderate intensity appeared in the region 1515 cm^{-1}; this is probably the band assigned by LECOMTE[14] to the enolic structure. Other bands tabulated (Table VIII) belong either to $-CH_3$ deformation or skeletal structure as reported by LECOMTE. The bands between 700 and 600 cm^{-1} character-

TABLE IX

INFRARED ABSORPTION BANDS OF Pr, Nd, Sm, Dy, Er AND Yb BENZOYLACETONATES.

BZA	*Pr-BZA*	*Nd-BZA*	*Sm-BZA*	*Dy-BZA*	*Er-BZA*	*Yb-BZA*	*Assignment*
	3320				3500sm		O–H stretching
	2340		2350	2335	3000sm		=C–H stretching
	1720sw						
1605sm	1600ms	1605ms	1600ms	1600ms	1600s	1600ws	Enol chelate
1570–60bw	1565ms	1562ms	1562ms	1575ms	1570m	1570ws	Perturbed carbonyl
	1550mb					1560	
	1529mb	1530–10 mb	1520–10m	1515ms	1525s	1520ws	Perturbed C=C
			1490ms	1490sh		1490ws	Phenyl
1460sw	1450ss	1460sh	1460ms		1460s	1460sh	
					1430sm		
					1400bm		
1365–60sh				1365sh	1370sh		
1310–1300 wb	1310w	1310w	1310ws	1310ws	1300s	1310w	
1260ms	1280w	1280wb	1280ms	1280sm	1260s	1285 (?)	=C–O
1200ms	1219w				1225bm		
1178ms	1175w		1175w	1180ws	1175m		
	1155w						
	1146w				1100w		
1082ms	1125w		1105w	1105sw			
1065ms	1070w		1075w	1070ws	1065w		
1063sw					1058w		
1025ms	1025sw	1030w	1025sw	1030sm	1025sm	1025w	
	995w		955ws	962sw	998w		
970–55 wb	875sw						
837ms	850–35w	845wb	845ws	845ms		845wb	
800w							
767ss	760–55w	760?	765–55w	775bm			
699ss	685w	730w	680 ?		695b	685 ?	

istic of the metals could not be recorded owing to instrument limitations. However, the band located at 720–722 cm^{-1} may have this origin because it is present in all the metal chelates.

Benzoylacetonates

The enol chelate band at 1640 cm^{-1} is present in all the chelates. The perturbed carbonyl at 1561 cm^{-1} is also present in all the chelates. These findings are in agreement with those of COLLMAN *et al.*[20].

Table IX summarises the absorption bands of pure benzoylacetone and several rare earth benzoylacetonates with the probable assignments.

Dibenzoylmethides

An intense band ascribed to perturbed carbonyl group was found at 1550 cm^{-1} in all the chelates (Pr, Nd, Sm, Eu, Tb, Dy, Er, Yb) in agreement with the work of COLLMAN *et al.*[20]. In other respects there was also fair agreement with the findings of

TABLE X

INFRARED ABSORPTION BANDS OF Pr, Nd, Sm, Eu, Tb, Dy, Er AND Yb DIBENZOYLMETHIDES

DBM	*Pr-DBM*	*Nd-DBM*	*Sm-DBM*	*Eu-DBM*	*Tb-DBM*	*Dy-DBM*	*Er-DBM*	*Yb-DBM*	*Assignment*
				3000w	3000w		3000w		
2348ws	2325w	2350w	2375w						
1740ws	1710ws								Free C=O
1600ms	1600sw	1600sm	1600sm	1600s	1600s	1610ss		1610ss	Perturbed C=O
							1590s		
	1550wb	1550mb	1550sm	1560s	1550s	1570–50sb	1550s	1560ss	
	1520sw			1550s	1545s		1545s	1535ss	Perturbed C=C
	1510sw			1520s	1510s	1515ss	1500s		
		1470sh	1470s	1475s	1475s	1490ss	1465s	1490ss	
		1445sh	1440sh	1450sm	1460w	1470ss	1450sm	1470sh	Phenyl
					1450s		1400m		
						1395sh			
				1390s	1400w		1390s		
					1390s				
1305bm	1305sh	1310w	1310w	1305bm					
					1300bm	1315sm	1300bm	1315sw	
1225ms	1220w	1220w	1220sw	1225b	1275m	1280sm			
					1225m	1220sm	1275m	1220sw	
1188ss				1185m	1175m		1175m		
1162?									
1099ws		1075b	1065w	1065m	1065m	1070w	1065m	1075mw	
					1048mb	1020s	1048m	1022sw	
1028bm		1020w	1020w	1050m	1018sm		1018sm		
				1025sm					
925mw				940w	940w		935w	943w	
880–70bw									
840w					850w		840w		
810w				815w	815w		815w		
785sm	770w	780w	770m	790w		782sw	810w	785w	
755ss			753w			750sm		755sm	
	722sw	720mb	720ms		708w	727sm			
707sm									
	692wb	685?	685?	689bs	685bs	685m	685bs	685ms	
679ss									

these authors. The absorption bands of pure dibenzoylmethane and several rare earth dibenzoylmethides, with probable assignments are summarised in Table X.

2-Thenoyltrifluoroacetonates

The thiophene band of TTA at 1587 cm^{-1} was not present in any of the chelates. The perturbed carbonyl shown in the copper chelates at 1570 cm^{-1}, was also absent in the rare earth chelates, but the thiophene band which appears at 1508 cm^{-1} in copper chelates was observed between 1510 and 1515 cm^{-1} in the rare earth chelates. The 1085 cm^{-1} thiophene band also appeared in the chelates. The C—F vibration at 1140 cm^{-1} in the reagent was present undisturbed in all the chelates. The second C—F band at 1067 cm^{-1} showed absorption at 1075 cm^{-1}, in the reagent and at 1060–1065 cm^{-1} in the chelates. Table XI gives the absorption bands of thenoyltrifluoroacetone and several rare earth chelates, with probable assignments.

TABLE XI

INFRARED ABSORPTION BANDS OF Nd, Sm, Tb, Dy, Er AND Yb THENOYLTRIFLUOROACETONATES

TTA	*Nd-TTA*	*Sm-TTA*	*Tb-TTA*	*Dy-TTA*	*Er-TTA*	*Yb-TTA*	*Assignment*
3520ss							
3202w							O—H stretching
2402mw		2350w				2350w	Carbonyl
1700ss							
1680ss	1620ss	1610ss	1600s	1620ss	1600s	1615ss	Enol chelate
1590w							
1570sh							
1550sm	1540ms	1540ms	1530sm	1540ms	1540sm	1550ms	Perturbed carbonyl
	1510ws	1515ms	1500w	1510ws	1500w	1515ws	Thiophene
1492ss		1465ss	1450w		1450w		
1400ms	1412ss	1415ss	1400s	1415sm	1400s	1415ss	Thiophene
1365ms	1360wb	1360ms	1350ms	1360ms	1350ms	1360ms	
1299ms	1300ss	1300ss	1300s	1310ss	1300s	1310ss	
1275mw	1250ms	1250ms	1240mw	1250ms	1245m	1260ms	
	1232ms	1230ms	1220mw	1230ms	1225mw	1232ms	
1205bm							
	1185ss	1190ms	1189m	1190ms	1189m	1185ms	
1190bm	1139ss	1140ss	1150s	1135ss	1150s	1145ss	C—F vibration
1140sm							
1108sm							
1095sh	1085w	1085ws		1080ws	1060sw	1080ws	Thiophene
	1062ms	1062ms		1060ms		1065ms	C—F vibration
1075sw							
		1040w	1055sw	1032ws		1035w	
						1010w	
990ss							
947ms							
935ms	935ms	935ms	930w	930ms	930w	935ms	
865sm							
860sm	860ms	862ms		859bm		862sm	
848w			830w	848ws	830w		
			820w		820w		
803w	788ms	790ms	810w	785ms	810w	788ms	
			800w				
765sh	770ms	770ms		770ws		770ws	
748ss		752ws		750w		750ws	
	720mb	720bs		720b		725–20ms	
	692wb	695ws		695ws		692ws	
685mb	680ws	682sm	687wb	685bw	687b	682sb	

Dithenoylmethides

The enol chelate band which appeared at 1645 cm^{-1} in pure dithenoylmethane was absent in the Nd and Er chelates. The thiophene bands at 1587 cm^{-1} and 1080 cm^{-1} were present in these chelates, but the second thiophene absorption at 1510 cm^{-1} varied between 1520 and 1490 cm^{-1}. There were no other significant features in the spectra.

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SUMMARY

The chelates of various rare earths with acetylacetone, benzoylacetone, dibenzoylmethane, 2-thenoyltrifluoroacetone and dithenoylmethane were prepared and some of their physical properties noted. The ultraviolet absorption spectra in various non-aqueous solvents were measured. Absorption measurements in the visible region showed alterations in absorption intensities and resolution in some of the principal bands, depending on the solvent. The infrared spectra were measured and compared with literature data.

RÉSUMÉ

Les auteurs ont préparé et examiné quelques propriétés physiques de chélates de diverses terres rares avec acétylacétone, benzoylacétone, dibenzoylméthane, 2-thénoyltrifluoroacétone et dithénoylméthane. On a mesuré les spectres d'absorption dans divers solvants non-aqueux. Dans le visible, on observe des variations d'intensités d'absorption suivant le solvant. Les spectres dans l'infra-rouge ont été mesurés et comparés aux valeurs données dans la littérature.

ZUSAMMENFASSUNG

Die Chelate verschiedener Seltener Erden mit Acetylaceton, Benzoylaceton, Dibenzoylmethan, 2-Thenoyltrifluoroaceton und Dithenoylmethan wurden hergestellt und einige ihrer physikalischen Eigenschaften ermittelt. Es wurden die UV-Spektren in verschiedenen nichtwässrigen Lösungsmitteln gemessen. Absorptionsmessungen im sichtbaren Bereich zeigten Änderungen in den Absorptionsintensitäten, und dass die Auflösung einiger Banden vom Lösungsmittel abhängt. Die gemessenen IR-Spektren wurden mit Literaturwerten verglichen.

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AUTOMATIC RECORDING IN CONDUCTOMETRIC PRECIPITATION TITRATION OF CARBON DIOXIDE

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The performance of conductometric titrations may often be greatly facilitated by automatic recording of the titration curves. The arrangement for automatic recording of electrolytic conductivity described in this paper has primarily been worked out for the determination of carbon dioxide in air by conductometric titration against a known amount of strontium hydroxide. The titration is carried out in a special spiral absorber, furnished with electrodes, in which a small volume of the absorption liquid (usually 0.5 ml of a 5 mM strontium hydroxide solution) is circulated by a stream of the air to be analysed[1,2]. The determination of the amount of carbon dioxide absorbed is based on measurements of the decrease in the conductivity of the hydroxide. These measurements were originally performed with a manually operated Wheatstone bridge.

In the analysis in question, the amount of carbon dioxide absorbed is equivalent to the amount of strontium hydroxide which is precipitated as carbonate, and as the volume of the liquid does not change measurably during the titration, the amount of carbon dioxide absorbed is also proportional to the decrease in the concentration of the hydroxide. The recording of a titration curve which correlates the remaining concentration of the hydroxide with time would therefore be appropriate.

The purpose of the experimental study on which the procedure described below is based was to establish a graphic record of some function of the conductivity which, with as close approximation as possible, would be proportional to the concentration of the strontium hydroxide solution.

The recordings were made by commercially available rectilinear d.c. potentio-

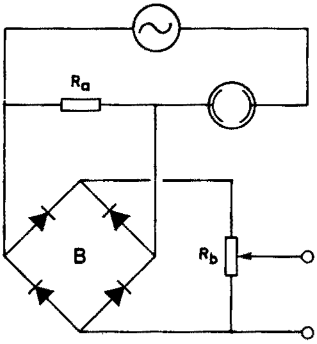

Fig. 1. For explanation, see text.

meter strip-chart recorders with 10-mV input span. The repeatability of the recorders used was better than ± 0.35% of span. In principle, the record was obtained by the arrangement illustrated in Fig. 1. Alternating current was passed through the electrode cell in series with a resistor, R_a. The voltage drop across R_a was rectified by the full-wave rectifying bridge, B, loaded with the resistance of the potentiometer, R_b, by means of which the resultant d.c. voltage, which is a function of the conductivity of the electrolyte in the cell, was adjusted to match the input of the strip-chart recorder.

With a rectifying bridge made of suitable diodes, and after selection of suitable values of R_a and R_b, it proved feasible to obtain a fairly linear relationship between the d.c. voltage registered and the conductivity to be determined in the range between 100% and about 20% of an initial conductivity of about $2 \cdot 10^{-4}\ \Omega^{-1}$, which represents the order of magnitude of the conductivity of a 5 m*M* strontium hydroxide solution measured with the electrodes of the above-mentioned spiral absorbers. However, with this simple arrangement the voltage recorded was not proportional to the conductivity.

Experiments revealed, however, that by replacing R_a with a suitable voltage-dependent resistor, the non-linearity of the rectifying diodes could be compensated so that not only was the linear relationship between the d.c. voltage recorded and the conductivity improved but also changed so that by adjustment of R_b, the record could be made closely proportional to the conductivity over a wide range. For practical reasons, the influence of minor temperature changes on the diodes and on the conductivity of the electrolyte was reduced by means of thermistors.

The final arrangement reached after many experiments is shown in Fig. 2. The diagram of the oscillator is given in Fig. 3.

Different strip-chart d.c. recorders were used. The Varian model G-11A recorder with an input voltage span of 10 mV, and the Beckman linear laboratory potentiometer recorder with input span adjustable between 8.5 and 105 mV were very suitable. Chart speeds of about 6 in./h were suitable for the analyses, whereas for the adjustment of the arrangement by means of a resistance box inserted instead of the electrode cell, a higher chart speed of about 30 in./h was more convenient.

The oscillator was fed with 12 V d.c. from a 6-cell lead accumulator with a capacity of about 36 A-h. As the discharge current was only about 40 mA, the d.c. voltage of the accumulator remained practically constant for several days. When the arrangement had been in continuous use for about a fortnight, the accumulator was charged during the week-end. The accumulator was shunted with a resistor of 300 Ω corresponding to a constant drain of about 40 mA and charged with a current of about 1.5 A for 10 h, at which time the charging was automatically interrupted by means of a time-switch; the accumulator was subsequently allowed to discharge across the shunt for at least 24 h before use for the analyses.

The oscillator produced a sine-wave output adjusted to 4.5 V and a frequency of about 600 c/s. At a constant load, the output voltage became constant in less than 1 h. The output voltage was slightly dependent on the external load, but this proved to be of no significance in the measurements.

An output voltage of the oscillator of about 4.5 V was chosen as a compromise. If it is essentially higher, the heating of the electrolyte caused by the current may under the prevailing conditions significantly influence the accuracy of the measurements. If it is lower, it becomes difficult to obtain maximum approach to the linearity

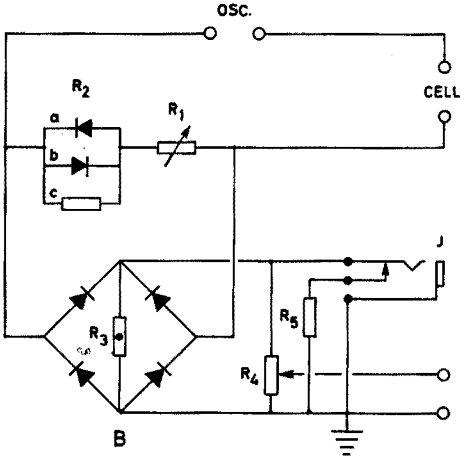

Fig. 2. Arrangement for creating a d.c. voltage signal which can be adjusted to be proportional either to the conductivity or to the concentration of an electrolyte. It is mounted in a metal case which is connected to earth. *Osc.* Input terminals for the oscillator. *Cell.* Terminals for the electrode cell of the spiral absorber. *B.* Rectifying bridge with 4 diodes. The rectifying elements used are Telefunken diodes, OA 182. R_1. Resistor, variable between 0 and 109 Ω. Two decades of standard carbon resistors are used. R_2. Voltage-dependent resistance composed of two diodes, R_{2a} and R_{2b}, and one ordinary resistor, R_{2c}. They are all connected in parallel, the diodes with opposite polarity. The diodes are of the same type as those used in the rectifying bridge, Telefunken OA 182. R_{2c} is connected by plugs to sockets placed in the roof of the box, so that it can easily be exchanged. R_{2c} must be adjusted to match the range of conductivities to be measured and is replaced by a variable resistor during this adjustment. When the same solution of hydroxide is used for repeated measurements with the same cell, or with cells with nearly identical cell constants, the same R_{2c} can be used. R_3. Resistance with negative temperature coefficient for compensating the temperature dependence of the diodes. Two Philips N.T.C. resistors type B8 320 01 P/500E, connected in series; the combined resistance at 23° is about 1100 Ω. The individual N.T.C. resistors should be selected to provide optimum temperature compensation as described in the text. In case of overcompensation an ordinary resistor (in practice 50 Ω to 100 Ω) may be placed in series with the N.T.C. resistors. R_4. Potentiometer, 5000 Ω, for adjustment of the output voltage to match the input of the recorder. R_5. Resistor, about 700 Ω, selected to be equal to the temperature-dependent resistor R_6 (see below) at ordinary room temperature (23°). *J.* "Jack" socket for connection of R_6. When the "jack" is inserted, R_5 becomes disconnected. R_6. Resistor with negative temperature coefficient to compensate for the influence of minor temperature changes upon the conductivity of the strontium hydroxide solution (1.7% per °). R_6, which is not shown in the diagram, may be connected by an unscreened twin-lead cable; it should be placed adjacent to the electrode cell of the spiral absorber during the measurements. R_6 consists of two Philips N.T.C. resistors, type B8 320 01 P/1K3, connected in parallel. They should be selected individually for optimum compensation as described in the text.

of the record. The frequency should at least be about 500 c/s to make it possible to carry out the conductivity measurements with uncoated platinum electrodes, which is desirable in the titrimetric determination of carbon dioxide (*cf.*[2]).

The rectifying characteristics of the six OA 182 diodes used in the arrangement may exhibit minor differences. However, any selection of the diodes is not worthwhile. Nine out of ten sets of unselected OA 182 diodes proved to give records which could not be further improved by selecting the diodes with respect to equality of the current–voltage characteristics.

Several diodes of other types were tested, but they all appeared to be inferior to the OA 182 for the present application.

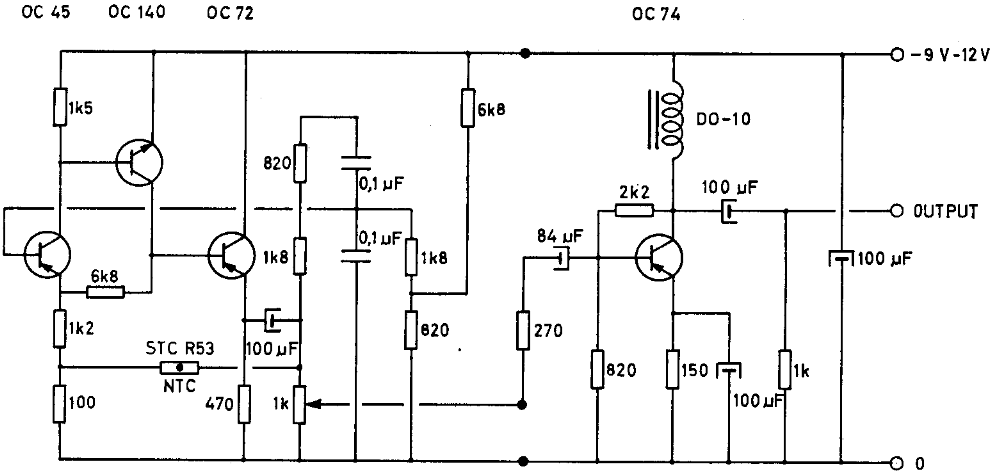

Fig. 3. In the left part of the figure is shown a three-transistor Wien-bridge phase-shift oscillator, which has been described by MULLARD, LTD.[3]. The output voltage from this oscillator is amplified by a choke-coupled class A output stage provided with a large negative feedback from collector to base. The output voltage which is adjusted to 4.5 V is very stable against variations in the supply voltage and in the external load. The frequency, about 600 c/s, is controlled by the two 1.8 kΩ resistors and the two 0.1 F capacitors. The choke (Do-10) has an inductance of approximately 0.2 H and a d.c. resistance of 10 Ω. Standard tolerance resistors and capacitors are used.

Adjustments

Before measurements of conductivities and concentrations could be carried out, certain adjustments were needed.

The oscillator and the recorder (with about 10-mV input span) were connected to the arrangement described in Fig. 2. The "jack" plug for connecting R_6 was not inserted. At the terminals for the cell was plugged in the cable which was used for connecting the cell. An unscreened twin-lead cable, length about 50 cm, served for this purpose. The peripheral ends of the cable were left unconnected corresponding to a cell resistance of infinity. The zero line of the graph was then adjusted by means of the zero control knob of the recorder.

After a lapse of at least 30 min for "heating up", a resistance box with 6 decades, accuracy ± 0.1%, was connected to the peripheral ends of the above-mentioned cable to replace the electrode cell during the adjustments.

Another resistance box adjustable between 1000 Ω and 10,000 Ω was connected to the sockets for R_{2c} to replace the fixed R_{2c} during the adjustment.

Adjustments for obtaining a graph with optimum proportionality to conductivity. The 6-decade precision resistance box replacing the electrode cell was adjusted to a resistance, R_{xo}, which, within ± 10%, was equal to the initial resistance encountered in the conductometric analysis. R_{xo} should be within the range of 2000–12,000 Ω. The optimum values of R_1 and R_2 for linear and proportional recording of decreasing conductivities were then determined as follows.

R_1 was provisionally put at 40 Ω, and R_{2c} at about 50% of R_{xo}. By means of R_4 the recorded graph was adjusted to full deflection (100%), and the appropriate values of R_1 and R_{2c} were determined which corresponded to the correct recording of $R_x = 2 \cdot R_{xo}$ and $5 \cdot R_{xo}$ (50% and 20%, respectively).

If the recorded level corresponding to $2 \cdot R_{xo}$ was below 50%, R_1 had to be reduced; if it was above 50%, R_1 had to be increased. If the record corresponding to $5 \cdot R_{xo}$ was below 20%, R_{2c} had to be increased; if it was above 20%, R_{2c} had to be reduced. Whenever R_{2c} was changed, R_1 had to be redetermined. The 100% level corresponding to R_{xo} had to be readjusted after any change of R_1 or R_{2c}.

TABLE I

ACCURACY OF THE CONDUCTIVITY MEASUREMENTS

Recording % of full scale	*Conductivities as percentages of the conductivity which corresponds to full-scale deflection*			
	R_{xo} = 2,000[a]	4,000	8,000	12,000
	R_1 = 40	51	70	88
	R_{2c} = 1,500	2,300	3,900	5,600
100.0	100.0	100.0	100.0	100.0
90.0	90.0	90.0	90.0	90.2
80.0	80.1	80.0	80.0	80.1
70.0	70.1	70.1	70.1	70.1
60.0	60.2	60.1	60.1	60.0
50.0	50.0	50.0	50.0	50.0
40.0	40.0	40.0	40.0	40.0
30.0	30.0	29.8	29.9	30.0
20.0	20.0	20.0	20.0	20.0
15.0	15.1	15.3	15.3	15.3
10.0	10.4	10.6	10.8	10.9
5.0	5.8	6.0	6.4	6.3
0.0	0.0	0.0	0.0	0.0

[a] Values given in ohms

Table I shows a typical set of results obtained with the arrangement described. It is seen that the maximum difference between recorded value and conductivity within a wide range did not exceed ± 0.3% of the conductivity corresponding to full-scale deflection, which was within the reproducibility of the recorders claimed by the makers.

For the tabulated results, various initial resistances, R_{xo}, equal to 2, 4, 8, and 12 kΩ, selected from a precision resistance box were recorded as 100% (full-scale deflection). The resistances, R_x, required to give the records indicated in the left column were measured by means of the resistance box; the conductivities as percentages of the corresponding initial conductivities, $R_{xo}/R_x \cdot 100$, are given in the following columns.

Adjustments for recording a graph, the level of which is closely proportional to the decreasing concentration of 5 mM strontium hydroxide during the uptake of carbon dioxide. The equivalent conductivity of electrolytes in aqueous solution decreases with increasing concentration due to interaction between the ions.

If it is assumed that the equivalent conductivity of solutions of strontium hydroxide is equal to $\Lambda\,(1 + 0.6c - 0.88\sqrt{c})$, where Λ is the limit of the equivalent conductivity at zero concentration and c the equivalent concentration of the hydroxide, the specific conductivities of the strontium hydroxide solutions in question can be calculated.

Table II shows the calculated specific conductivities of strontium hydroxide solutions (second column), which correspond to various concentrations of the hydroxide (first column). They are expressed as percentages of the specific conductivity and of the concentration of a 5 m*M* solution, respectively.

TABLE II

ACCURACY FOR DETERMINATION OF STRONTIUM HYDROXIDE

Concentrations of $Sr(OH)_2$, % of 5.0 mM/l	*Calculated conductivities as percentages of the specific conductivity of a 5 mM solution*	*Conductivities, determined with the resistance box, which are recorded by the figures in the left column*			
		R_{xo} = *2,000*[a] R_1 = *47* R_{2c} = *1,500*	*4,000* *61* *2,300*	*8,000* *84* *3,900*	*12,000* *107* *5,600*
100.0	100.0	100.0	100.0	100.0	100.0
90.0	90.38	90.4	90.4	90.4	90.6
80.0	80.70	80.9	80.9	80.8	81.0
70.0	70.95	71.1	71.0	71.1	71.2
60.0	61.13	61.3	61.3	61.3	61.4
50.0	51.24	51.2	51.4	51.2	51.5
40.0	41.25	41.3	41.2	41.0	41.3
30.0	31.16	31.2	31.1	31.1	31.1
20.0	20.95	21.0	21.0	21.0	21.0
15.0	15.80	16.1	16.0	16.0	16.2
10.0	10.60	10.9	11.1	11.2	11.4
5.0	5.34	6.0	6.4	6.6	6.6
0.0	0.00	0.0	0.0	0.0	0.0

[a] Values given in ohms

In order to obtain a record the level of which was proportional to the concentration instead of the conductivity, provision had to be made for registration of the conductivities given in the second column by the corresponding figures in the first column.

This was done as follows. Starting from the values of R_1 and R_{2c} selected to give proportionality between registration and conductivity, R_1 was increased until a resistance of $2 \cdot R_{xo}$ was recorded as 48.7 ± 0.1% of the initial conductivity. R_{2c} was not changed. With these values of R_1 and R_2, the level of the recorded graph appeared to be proportional to the concentration of the strontium hydroxide with an error which within a wide range (100–15%) did not exceed ± 0.4% of the initial conductivity of the hydroxide (Table II, columns 3–6).

In a subsequent paper, it will be demonstrated that when the conductometric analyses are performed by means of the above-mentioned spiral absorbers[2] maximum accuracy is obtained when $2 \cdot R_{xo}$ is recorded as about 48.2%. This is probably due to changes in the concentration of the hydroxide caused by adsorption on the extensive inner glass surfaces of the spiral absorber.

Adjustment for best possible compensation of the influence of temperature changes on the performance of the diodes. When the temperature is increased, the resistance of the diodes decreases, and with the arrangement in question the rectified voltage increases by 1.0–1.5% per ° depending on the values of R_1, R_{2c}, and R_x. By selection of the individual compensating thermistors used to make R_3, this temperature dependence could be greatly reduced. However, as it was influenced also by the changing R_x, it could not be completely cancelled. The above-mentioned accuracy of the measurements was obtained only when the ambient temperature did not fluctuate by more than ± 1.0°; moreover, because of the possibility of temperature differences between the temperature-dependent resistors (including the diodes), this accuracy was obtained only if the change of temperature was slow, *i.e.* less than about 1.0° during 60 min.

Adjustment for compensating the influence of temperature changes on the conductivity of the strontium hydroxide solutions (+1.7% per °). By individual selection of the thermistors incorporated in R_6, it was possible to obtain a very good compensation of the influence of the temperature dependence of the conductivity of the electrolyte upon the recording.

The combined temperature compensation obtained by means of R_3 and R_6 can easily be checked by experiments. It should not exceed the error for the correction of the temperature dependence of the diodes by means of R_3.

The author is indebted to Dr. FOLMER NIELSEN KUDSK for the diagram of the oscillator.

SUMMARY

A fairly simple and inexpensive arrangement is described by which conductivities of electrolytes can be graphically recorded by means of commercially available strip-chart d.c. potentiometer recorders.

The level of the graph can be arranged to be proportional either to the conductivity or to the concentration of dilute solutions of strontium hydroxide.

RÉSUMÉ

L'auteur propose un dispositif simple et peu coûteux pour le titrage conductométrique de l'anhydride carbonique, avec enregistrement automatique. La courbe peut être tracée de façon à être proportionnelle soit à la conductivité, soit à la concentration de la solution d'hydroxyde de strontium.

ZUSAMMENFASSUNG

Es wird eine einfache und billige Anordnung beschrieben, mit der Leitfähigkeiten von Elektrolyten mittels eines kommerziellen automatischen Registriergeräts aufgezeichnet werden können. Die graphische Darstellung kann entweder proportional der Leitfähigkeit oder proportional der Konzentration von verdünnten Strontiumhydroxidlösungen erfolgen.

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TIN(II) CHLORIDE IN GLYCEROL AS A TITRIMETRIC REAGENT IN CARBONATE MEDIA

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Tin(II) chloride as a reducing titrant is generally used in hydrochloric acid solutions. The instability of tin(II) to atmospheric oxygen in such media is well known; it is necessary to standardize the solution each time it is used, or to store it under an inert atmosphere as proposed by SZABÓ AND SUGAR[1]. Some years ago, SLETTEN AND BACKS[2] found that tin(II) chloride dissolved in glycerol had the same reducing power as an aqueous solution, for the colorimetric determination of phosphate. According to HARING AND WALTON[3], glycerol acts as a negative catalyst for the atmospheric oxidation of tin(II). Tin(II) chloride is readily soluble in glycerol and the reducing properties of such solutions appear to be the same as those of hydrochloric acid solutions for several reactions. The titre of the glycerol solutions remains constant for several months when the solutions are stored in properly stoppered vessels.

The practical utilization of these glycerol solutions as a reducing titrant may be made difficult by their viscosity. However, solutions should flow easily in burets if neutral, twice-distilled glycerol of the grade specified below is used; if necessary the solution can be made more fluid by the addition of absolute ethanol, though not more than one part of ethanol to three of glycerol should be added.

The reagent prepared in this way serves, of course, only for the determination of oxidants which do not react with the solvent. In acidic media, in which tin(II) chloride is commonly used, most oxidants react with glycerol, and better still with a glycerol–ethanol mixture. But in alkaline media, generally speaking, such reactions either do not occur, or occur very slowly, whereas the reducing power of tin(II) is stronger in alkaline than in acidic media. However, the media must not be too alkaline, otherwise stannite tends to decompose to Sn and SnO_3^{2-}, or to precipitate as SnO.

Earlier work[4] showed that in solutions saturated with sodium carbonate, tin(II) does not decompose even at boiling temperatures; that the influence of atmospheric oxygen is less than in acidic or strongly alkaline media; and that with low concentrations of tin(II) there is no precipitation of basic salts or hydroxides. The presence of glycerol favours this absence of precipitation, due to its complexing properties[5].

Standardization of 0.1 N tin(II) chloride solutions in glycerol. Hydrochloric acid solutions of tin(II) chloride are usually standardized in strongly acidic medium against potassium dichromate, bromate, iodate or ferricyanide[1]. All these oxidants react to some extent with glycerol in acidic medium. However, neither potassium dichromate nor ferricyanide reacts with glycerol in a saturated carbonate medium, whereas they are reduced to chromium(III) and ferrocyanide by tin(II); iodate and bromate are not reduced by tin(II) in such a medium.

Accordingly, tin(II) solutions can be standardized against ferricyanide or potassium dichromate, which are both primary standards, and, of course, ferricyanide and chromate ions can be determined in a carbonate medium.

Standardization with potassium ferricyanide. Many years ago, attempts were made to use potassium ferricyanide for the standardization of tin(II) solutions in strongly alkaline media[6,7] but difficulties were encountered because of the rapid atmospheric oxidation of tin(II) in such media and because of the disproportionation of the stannite ion. More recently[8], potassium ferricyanide was determined in weakly alkaline media with hydrochloric acid solutions of tin(II), in the presence of sodium pyrophosphate and sodium triphosphate as complexing agents for tin(II).

In the present work, the solution of tin(II) in glycerol was added to the carbonate solution of ferricyanide and no special precautions in regard to addition of complexing agents or against atmospheric oxidation were necessary. The course of the titration was followed potentiometrically; the reactions were very rapid and proceeded stoichiometrically. The potential jump at the end-point was of the order of 195 mV for 0.05 ml of 0.1 *N* tin(II) solution with a platinum indicator electrode and a saturated calomel reference electrode.

Ferricyanide can act as its own indicator, becoming decolorized at the equivalence point, but the end-point is not clear; several of the redox indicators which have been proposed for use in alkaline media[9] were tested, but none of the end-points obtained was very satisfactory. However, it was found that the complex ion $Ag(NH_3)_2^+$ was reduced to elementary silver by glycerol solutions of tin(II) at a potential lower than that of the reduction of ferricyanide. Thus, when the ferricyanide had been reduced, a brownish-yellow tint gave an excellent indication of the end-point.

During the titration, silver ferrocyanide was precipitated so that the reduction of ferrocyanide was favored because of the increase in the oxidation potential of the ferricyanide–ferrocyanide system.

The equations of the processes during the titration and at the end-point would be:

$$2\,Fe(CN)_6^{3-} + HSnO_2^- + 8\,Ag(NH_3)_2^+ + 2\,OH^- \rightarrow 2\,Ag_4Fe(CN)_6\downarrow + \\ + HSnO_3^- + 16\,NH_3 + H_2O \quad (1)$$

$$2\,Ag(NH_3)_2^+ + HSnO_2^- + 2\,OH^- \rightarrow 2\,Ag\downarrow + HSnO_3^- + 4\,NH_3 + H_2O \quad (2)$$

Standardization with potassium dichromate. There is no information in the literature on the determination of tin(II) with dichromate, or *vice versa*, in alkaline media.

In carbonate solution, tin(II) reduced chromium(VI) to chromium(III) at room temperature. When a solution of tin(II) chloride in glycerol was used in the presence of ammonia, the reaction was quantitative and there was no precipitation of $Cr(OH)_3$. When the end-point was detected potentiometrically, a large potential jump of about 350 mV was obtained at the theoretical equivalence point with 0.05 ml of 0.1 *N* tin(II) solution.

The reaction can be represented as follows:

$$2\,CrO_4^{2-} + 3\,HSnO_2^- + 12\,NH_4OH \rightarrow 2\,Cr(NH_3)_6^{3+} + 3\,HSnO_3^- + \\ + 10\,OH^- + 7\,H_2O \quad (3)$$

It is quite possible that complexes containing glycerol, more complicated than the simple ammoniacal complex, were formed; red-violet solutions can be obtained by addition of glycerol to chromium(III) in the presence of ammonia[10]. In the present work, a change in colour from green to rose-violet was found to coincide with the end-point. However, this change of colour was not very sharp, so that the end-point had to be detected either potentiometrically or with a redox indicator. Among all the indicators tried, iron(II)–dimethylglyoxime[11] was the most suitable; the indicator was added at the beginning of the determination, being decolorized by the chromate, and when all the chromate had been reduced, the tin(II) reduced the indicator, the red colour reappearing. The end-point was quite sharp with a change of colour from greyish green to pale clear purple. In agreement with literature data[12,13], it was found that alcohols were not oxidized by chromium(VI) in the proposed alkaline medium even at boiling temperature.

EXPERIMENTAL

Reagents

Potassium ferricyanide, 0.1 N. Prepare from the pure salt (analytical grade), previously dried at 100°.

Potassium dichromate, 0.1 N. Prepare from the pure salt (analytical grade), previously dried at 110°.

Tin(II) chloride in glycerol, 0.1 N. Add the theoretical quantity of the $SnCl_2 \cdot 2H_2O$ to 750 ml of pure, twice-distilled glycerol (Merck reagent grade, d 1.221) and leave at room temperature until dissolution is complete (about 1 h); do not agitate strongly. If necessary, dilute the solution to 1 l with absolute ethanol and homogenize the mixture. If the glycerol is fluid enough then use glycerol for the dilution.

Silver indicator solution. Add sufficient concentrated ammonia solution to 0.1 *N* silver nitrate to form the ammine complex.

Dimethylglyoxime indicator. To two drops of 0.02 *M* iron(II) sulphate add 4 drops of ethanolic 1% dimethylglyoxime solution and then add ammonia solution until an intense red colour appears[11]. No indicator correction was necessary because the amount of chromium(VI) required for the oxidation was equivalent to the amount of tin(II) necessary for the reduction.

Procedures

Titration of ferricyanide. To a known volume of ferricyanide, add *ca.* 50 ml of a saturated solution of sodium carbonate together with a little solid sodium carbonate; add 2 ml of the ammoniacal silver indicator. Titrate with the tin(II) chloride solution while stirring mechanically or magnetically, until the white suspension acquires a brownish-yellow tint.

Titration of dichromate. Proceed as above but add 2 ml of concentrated ammonia solution, and 5 drops of dimethylglyoxime indicator. Results for the standardization of a tin(II) solution against potassium dichromate and ferricyanide are given in Table I.

TABLE I

STANDARDIZATION OF TIN (II) SOLUTION AGAINST POTASSIUM DICHROMATE AND FERRICYANIDE

0.1 *N* $K_3Fe(CN)_6$ taken (ml)	$SnCl_2$ used (ml)	Normality $SnCl_2$ found	0.1 *N* $K_2Cr_2O_7$ taken (ml)	$SnCl_2$ used (ml)	Normality $SnCl_2$ found
5.00	5.60	0.0893	5.00	5.60	0.0893
10.00	11.15	0.0897	10.00	11.10	0.0898
15.00	16.70	0.0898	15.00	16.80	0.0894
20.00	22.30	0.0897	20.00	22.40	0.0896
25.00	27.90	0.0896	25.00	27.80	0.0899
30.00	33.50	0.0896	30.00	33.40	0.0898

TABLE II

DETERMINATION OF DICHROMATE IN THE PRESENCE OF REDUCING AGENTS

(10.00 ml of 0.1 *N* dichromate was used throughout)

Reductant present[a] (ml)	0.0985 *N* $SnCl_2$ used (ml)	0.1 *N* $K_2Cr_2O_7$ found (ml)	Absolute error (ml)	Relative error (%)
Na_2SO_3				
5	10.15	10.00	—	—
10	10.20	10.05	0.05	+0.5
15	10.20	10.05	0.05	+0.5
20	10.20	10.05	0.05	+0.5
30	10.15	10.00	—	—
40	10.15	10.00	—	—
50	10.20	10.05	0.05	+0.5
KSCN				
5	10.20	10.05	0.05	+0.5
10	10.15	10.00	—	—
15	10.15	10.00	—	—
20	10.15	10.00	—	—
30	10.20	10.05	0.05	+0.5
40	10.15	10.00	—	—
50	10.15	10.00	—	—
KI				
5	10.10	9.94	0.06	−0.6
10	10.15	10.00	—	—
15	10.15	10.00	—	—
20	10.15	10.00	—	—
30	10.15	10.00	—	—
40	10.20	10.05	0.05	+0.5
50	10.20	10.05	0.05	+0.5

[a] As a 5% solution.

APPLICATIONS

Since the chromate ion is compatible with numerous reducing agents in alkaline media but not in acidic media, the described procedure offers a suitable and useful method for the determination of chromate in such solutions, which generally require laborious or indirect procedures of analysis. Another application is the determination of chromium in materials which are not easily attacked by acids and require treatment with sodium peroxide and sodium carbonate. Chromium can be determined by the described method in the aqueous extract of the melt, without prior acidification, which can cause complications in some cases, after simple adjustment of the pH to 10–11.5. Some results obtained in the determination of chromate in the presence of variable quantities of sulphites, thiocyanates and iodides are given in Table II.

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SUMMARY

Tin(II) chloride solutions in glycerol are much more stable to light and atmospheric oxidation than the usual hydrochloric acid solutions, although the general reducing properties of the solutions are similar. In bicarbonate media, ferricyanide and chromate can be readily determined; some possible applications are outlined.

RÉSUMÉ

Les solutions de chlorure d'étain(II) dans le glycérol sont beaucoup plus stables à la lumière et à l'oxydation atmosphérique que les solutions habituelles dans l'acide chlorhydrique, bien que leurs propriétés réductrices soient semblables. Ferricyanure et chromate peuvent ainsi être dosés rapidement, en présence de bicarbonate.

ZUSAMMENFASSUNG

Zinn(II)-chloridlösungen in Glyzerin sind gegenüber Licht und atmosphärischer Oxydation wesentlich stabiler als die üblichen salzsauren Lösungen. Die allgemeinen reduzierenden Eigenschaften dieser Lösungen sind den salzsauren ähnlich. In einer bicarbonathaltigen Lösung können Ferricyanid und Chromat schnell bestimmt werden. Über einige mögliche Anwendungen wird berichtet.

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SUBMICRO METHODS FOR ANALYSIS OF ORGANIC COMPOUNDS

THE DETERMINATION OF THIOL GROUPS

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The thiol group is generally highly reactive and is of particular interest in biochemical analysis. Many colorimetric methods are available for the determination of thiols but none is widely applicable[1]. Of the various titrimetric methods[1], titration with silver(I) solution with amperometric indication of the end-point[2] appears to be most often used, but with some compounds anomalous results can be obtained because a 1 : 1 complex is not always formed; further, the instrumentation needed for the amperometric technique made it unattractive for submicro work. Submicro analysis has never been visualized as required for extensive routine application and so wherever possible, the methods have been kept as simple as possible, particularly with regard to instrumental requirements. Accordingly, attention was concentrated on the iodimetric and mercurimetric procedures. In both cases, the visual end-points of similar titrations were known to be satisfactory for microgram analyses.

Iodimetric methods

Thiol groups are normally oxidized to the disulphide by iodine[3]; usually the excess of iodine is titrated, but direct titration is successful for some compounds, *e.g.* glutathione[4]. Direct titration proved unsatisfactory for submicro work because of indistinct end-points and the back-titration technique was therefore preferred. Many compounds were insoluble in water, but soluble in ethanol; as on the macroscale, the maximum tolerable concentration of ethanol for the starch–iodine end-point was found to be 30%.

The optimum conditions were established[5] to be as follows: the 40–80 μg sample was dissolved in 0.2 ml of water (or water and ethanol) and 0.015 ml of 5 N sulphuric acid and 0.1 ml of a freshly prepared 10% solution of potassium iodide were added followed by exactly 100 μl of 0.01 N iodine solution; after one minute, the excess of iodine was titrated with 0.01 N thiosulphate in presence of Thyodene indicator. With proper precautions in technique, this method gave excellent results for reduced glutathione (an average recovery of 99% with a maximum relative error of ± 2%), but other compounds gave exceedingly variable results. Cysteine hydrochloride was apparently oxidized to the sulphoxide (*cf.* BICKFORD AND SCHOETZOW[6]) whereas the reactions of *o*-mercaptobenzoic acid and 2-mercaptoimidazole followed no

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well-defined course. With secondary and tertiary mercaptans, the formation of sulphenyl iodides as well as disulphides must be considered[7]. Further studies were therefore directed towards a more generally applicable procedure.

Mercurimetric methods

Several methods based on the formation of highly stable mercury mercaptides have been described[1,8]; the most promising for the microgram scale appeared to be that of FRITZ AND PALMER[8], in which the mercaptan is simply titrated with $5 \cdot 10^{-2}$–$5 \cdot 10^{-4}$ M mercury(II) perchlorate in neutral acetonic medium, the end-point being detected potentiometrically, photometrically or visually with thio-Michler's ketone [4,4′-bis(dimethylamino)thiobenzophenone] as indicator.

Thio-Michler's ketone as indicator

Preliminary tests on the microgram scale showed that good visual end-points could be obtained with $5 \cdot 10^{-3}$ M mercury(II) solutions in 1-ml volumes of acetone, benzene–acetone (2:3) and petroleum ether–acetone (2:3), the media which were previously recommended[8]. However, the indicator blank could not be determined because of very fleeting end-points, although the end-points were quite stable when samples were titrated and the results were satisfactory with no blank deduction. Better and more stable end-points were obtained in 1:4 water–ethanol solutions, and there was then no difficulty in determining the indicator blank. None of the compounds encountered in the present work was insoluble in ethanol and/or water and so this medium was used in all subsequent work. The conditions were not critical, provided that the compound was properly dissolved; the quantities of pyridine buffer and indicator specified under EXPERIMENTAL gave the best end-points. Because highly acidic mercaptans may form ketals with acetone[8], such compounds were neutralized before the addition of the acetonic indicator solution; this step had no effect on the accuracy of the results for other mercaptans.

Several methods for the standardization of the $5 \cdot 10^{-3}$ M mercury(II) perchlorate solution were compared. On the milligram scale, direct titration of mercury(II) with standard EDTA solution in the presence of pyridine buffer and thio-Michler's ketone indicator[8] gave essentially the same result (0.005140 ± 0.000015 M) as that obtained by adding excess of EDTA and back-titrating with magnesium chloride solution in the conventional way (0.005147 ± 0.00001 M). On the microgram scale, indistinct end-points marred the direct titrations; the indirect procedure (see EXPERIMENTAL) produced results in excellent agreement with the micro-method (0.005146 ± 0.000015). Standardization of the mercury(II) solution against sodium chloride[9] gave similar results (0.005153 ± 0.00002), which was surprising in so far as the mercurimetric titration of chloride is generally held not to be stoichiometric. The mercury(II) perchlorate solution maintained its titre for several months when properly stored.

The results obtained for a variety of compounds are shown in Table I. For all the pure solid materials examined, the average recovery was 99.85%; the maximum absolute error was ± 0.5% and the average error was ± 0.25% for 11 replicate determinations on reduced glutathione. With L-cysteine hydrochloride only the thiol group was determined; non-ionizable chlorine also showed no tendency to interfere. When sodium chloride or bromide was present there was a small consumption of

TABLE I

THIO-MICHLER'S KETONE AS INDICATOR

Compound	*Weight taken (μg)*	*SH found (%)*	*SH calcd. (%)*	*% Recovery*
Reduced glutathione (11 detns.)	50–80	10.68 (10.33–11.19)	10.76	99.3
L-Cysteine hydrochloride	52.40	20.76	20.94	99.1
	55.70	20.77		99.2
Thionalide	72.86	14.68	14.54	101.0
	92.68	14.47		99.5
o-Mercaptobenzoic acid	55.36	21.50	21.45	100.2
	68.95	20.91		97.5
2-Mercaptoimidazole	76.26	32.55	33.02	98.6
	81.24	33.49		101.4
2-Mercaptobenzothiazole	80.91	19.33	19.77	97.8
	59.49	20.01		101.2
4-Methyl-2-thiouracil	60.70	23.53	23.27	101.1
	75.97	23.28		100.0
p-Chlorothiophenol	—[a]	22.60	22.86	98.9
	—[a]	23.28		101.8
Glycol dimercaptoacetate	—[a]	31.27	31.46	99.4
	—[a]	31.73		100.9
Mercaptoacetic acid	—[a]	36.05	35.90	100.4
	—[a]	35.55		99.0

[a] A sample of *ca.* 5 mg was dissolved in aqueous ethanol under nitrogen and diluted to 100 ml; a 1-ml aliquot was taken for the titration.

titrant when no mercaptan was present, but in an actual determination the only effect was a slight decrease in the clarity of the end-point. Iodide and cyanide ions interfered badly. Reduced glutathione could be determined accurately in the presence of 100-μg amounts of L-cysteine and DL-methionine; probably much larger amounts could be tolerated. There was no interference from the heterocyclic sulphur in the thiazole analysed. In general the interferences seemed to follow the same pattern as on the milligram scale[8].

None of the compounds tested failed to react whether the mercaptans were primary, secondary or tertiary; however, when the SH– group was attached to a heterocyclic ring the titration had to be conducted at a slower rate and the end-points were a little sluggish, presumably because of tautomeric effects. In all cases, the mercaptan reacted with mercury(II) to form a 1:2 mercury(II)–thiol complex.

No method of weighing 50-μg samples of volatile, air-sensitive liquids has so far been devised. In order to check the reactions of such compounds, milligram samples were dissolved in aqueous ethanol in an air-free flask and aliquots containing about 50 μg were taken for immediate analysis.

Diphenylcarbazone as indicator

GREGG *et al.*[10] have reported that some mercaptans and aryl trityl sulphides can be directly titrated with mercury(II) nitrate solution in aqueous ethanolic media with the indicator and pH conditions commonly used for the mercurimetric titration of chloride. When the same conditions as those found satisfactory for the submicro titration of chloride[9] were used for mercaptans, excellent end-points were obtained for all the compounds examined. Various media were tested; the end-points were unsatisfactory in neutral and slightly acidic acetone or water, but good in 70–100% ethanol at an apparent pH of 3–3.5.

The results obtained for a selection of compounds are shown in Table II. For all analyses, the average recovery was 100.17% and the precision of the method was the same as that of the thio-Michler's ketone procedure. Peculiar results were obtained for glutathione and cysteine in that 1:1 complexes of mercury(II) with the compound were obtained, whereas these compounds formed 1:2 mercury(II)–thiol complexes when thio-Michler's ketone was used as indicator. The only other compound encountered which appeared to form the 1:1 complex when diphenylcarbazone was the indicator was 2-mercaptopyrimidine; the sample was very impure, but the results obtained agreed well when calculated on a 1:2 basis for the thio-Michler's ketone method and on a 1:1 basis for the diphenylcarbazone method. Various other heterocyclic thiols gave excellent results based on the formation of a 1:2 complex and there is no obvious structural reason for the anomalous behaviour of the pyrimidine. KOLTHOFF *et al.*[11,12] have shown, in polarographic and amperometric studies of the determination of thiol groups in proteins, that at pH 3, glutathione can form two complexes with mercury, $Hg(GS)_2$ and $Hg_2(GS)_2$, whereas at pH 9.2 only $Hg_2(GS)_2$ is formed; cysteine can also form several complexes. In the present work, there was no

TABLE II

DIPHENYLCARBAZONE AS INDICATOR

Compound	*Weight taken (μg)*	*SH found (%)*	*SH calcd. (%)*	*% Recovery*
Reduced glutathione[a]	70.74	10.81	10.76	100.5
	73.16	10.78		100.2
Cysteine hydrochloride[a]	72.89	20.49	20.98	97.7
	72.15	20.74		98.9
o-Mercaptobenzoic acid	88.80	21.29	21.45	99.3
	80.35	21.05		98.1
2-Mercaptoimidazole	50.97	33.06	33.02	100.1
	64.17	32.74		99.2
2-Mercaptobenzimidazole	84.89	22.42	22.02	101.8
	45.52	22.48		102.1
2-Mercaptobenzothiazole	73.59	19.84	19.77	100.3
	50.18	19.57		99.0
p-Chlorothiophenol	—[b]	22.83	22.86	99.8
	—[b]	23.20		101.5
Glycol dimercaptoacetate	—[b]	31.25	31.46	99.3
	—[b]	31.62		100.5
Mercaptoacetic acid	—[b]	36.35	35.9	101.3
	—[b]	35.85		99.9

[a] See text.
[b] See footnote to Table I.

difference in the reaction stoichiometry when the apparent pH was altered between 2.5 and 7.0; within this pH range, glutathione and cysteine gave clear-cut end-points corresponding to the 1 : 1 complexes when the carbazone was used as indicator and to the 1 : 2 complexes when the thioketone was used. Obviously, the difference in behaviour must be due to a large difference in the stability of the mercury(II)–carbazone and mercury(II)–thioketone complexes, the latter being formed much more readily. In aqueous ethanol at least, the stability of the various complexes must lie in the order $Hg(RS)_2 > Hg(TMK)_2 > Hg_2(RS)_2 > Hg(DPC)_2$; no actual data appear to be available for the stability constants of any of these complexes. From the series of compounds analysed it appears that the primary amino group plays by far the most important role in the formation of the 1 : 1 complexes, for mercaptoacetic acid and other compounds containing carboxyl groups formed only the 1 : 2 complexes (*cf.* KOLTHOFF *et al.*[13]) whichever indicator was used.

In the diphenylcarbazone method, chloride and bromide interfered quantitatively and this was a disadvantage compared with the thioketone method. When cysteine hydrochloride was analysed, the ionizable chloride was titrated quantitatively (in addition to the formation of the 1 : 1 complex with cysteine itself), whereas non-ionizable chloride was not titrated; as in the thioketone method, there was no interference from heterocyclic sulphur.

An attempt was made to use diphenylthiocarbazone (dithizone) as indicator in the titration of various thiols with mercury(II) solution. However, in all cases, the mercury(II)–dithizone complex was formed quantitatively before any of the thiols tested began to react, and the method appeared to be excellent for the determination of dithizone which acted as its own indicator. The various results appear to favour the suggestion that the dithizone complex is formed directly with the sulphur atom[14], whereas the diphenylcarbazone complex is formed through the oxygen and an adjacent nitrogen[15]; if two nitrogen atoms participated in each case, the behaviour of the indicators would be much more similar.

In conclusion, the diphenylcarbazone method has a mild advantage with highly acidic mercaptans in that no preneutralization is necessary; and where compounds form 1 : 1 complexes, there is a better calculation factor. However, the procedure with thio-Michler's ketone must be preferred for general purposes because of the uniformity of the reactions and the greater freedom from interferences.

EXPERIMENTAL

Apparatus

The Oertling QO1 microgram balance and accessories and the titration apparatus were as described previously[9]. Titrations were done in pyrex-glass test-tubes (*ca.* 65 × 16 mm) which were thoroughly cleaned and oven-dried before use. Apart from the titrant, all reagents were added from capillary dropping bottles which delivered drops of approximately known size.

Reagents

Mercury(II) perchlorate solution, 0.005 M. 2.8 g of mercury(II) perchlorate nonahydrate was dissolved in 0.1 *M* perchloric acid and diluted to 1 l with the same acid solution. The solution was filtered if necessary and stored in a brown glass bottle.

Thio-Michler's ketone solution, 0.01%. A 0.01% solution of the indicator (Eastman White-Label product) in acetone was stored in a brown glass dropping bottle which had been previously soaked in a stronger solution of the indicator and then rinsed with acetone. This solution was satisfactory for only 2–3 days.

Pyridine buffer, pH 6. This was prepared by adding AnalaR glacial acetic acid to pyridine (99%) until the pH was 6 measured with a pH meter.

Distilled water was boiled and then cooled under nitrogen. The organic solvents were of the purest grade obtainable; any dissolved oxygen was removed by bubbling a rapid stream of nitrogen through the solvent.

Standardization of mercury(II) perchlorate. A 200-µl aliquot of the solution was added to exactly 400 µl of standard 0.005 *M* EDTA, 0.5 ml of water being used to rinse the tips of the Agla burets. After the addition of *ca.* 0.2 ml of ammonia–ammonium chloride buffer (pH 10) and *ca.* 0.025 ml of freshly prepared 0.1% eriochrome black T in ethanol, the solution was back-titrated with 0.005 *M* magnesium chloride solution. Another 400-µl aliquot of the EDTA solution was titrated directly and the titre of the mercury(II) solution was calculated from the difference.

Alternatively, the solution was standardized against weighed 40–60 µg portions of pure sodium chloride[9].

Procedure with thio-Michler's ketone as indicator

The sample (40–80 µg) was dissolved in 0.2 ml of water and 0.8 ml of ethanol measured from hypodermic syringes. After the sample had been dissolved by stirring and heating if necessary, *ca.* 0.08 ml of pyridine buffer and 0.04 ml of the indicator solution were added. The solution was stirred for 30 sec and then titrated with standard mercury(II) solution to the end-point from clear yellow to blue under a "daylight" lamp; near the end-point, the titrant was added in 0.2-µl portions and the end-point was taken as the first appearance of a stable blue colour. When the titration was done in acetone medium instead of aqueous ethanol, the end-point was indicated by a change from vivid greenish-yellow to blue.

Blank determinations were done in exactly the same way but without a sample; values of *ca.* 3 µl were usually found for aqueous ethanol media.

Acidic mercaptans were neutralized in aqueous and/or ethanolic solution with 0.02 *M* sodium hydroxide in presence of 0.01 ml of an ethanolic 0.1% solution of phenolphthalein. This had to be done before addition of any acetone.

Procedure with diphenylcarbazone as indicator

The weighed sample was dissolved in aqueous ethanol as above and *ca.* 0.015 ml of aqueous 0.03% bromophenol blue, 0.015–0.02 ml of 0.05 *M* nitric acid and 0.02–0.03 ml of ethanolic 0.5% diphenylcarbazone solution were added. After being stirred, the solution was titrated as described above to the end-point from clear yellow to the first tint of pink.

Blank determinations in this procedure usually amounted to 1–2 µl of titrant. No neutralization of acidic mercaptans was required.

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SUMMARY

Several methods are described for the determination of thiol groups in organic samples weighing only 50 μg. Iodimetric methods were not widely applicable but the mercurimetric method of FRITZ AND PALMER in which thio-Michler's ketone serves as indicator was readily scaled down and gave excellent results (error ± 0.5% absolute) for all compounds tested. Diphenylcarbazone was also tried as the indicator; the procedure was satisfactory for most materials, but some anomalous results were obtained.

RÉSUMÉ

Plusieurs méthodes sont décrites pour le dosage des groupes thiol dans des échantillons de substances organiques, pesant seulement 50 μg. Les méthodes iodométriques ne sont pas toujours applicables; par contre, la méthode mercurimétrique de FRITZ ET PALMER, dans laquelle la thiocétone Michler sert d'indicateur a donné d'excellents résultats pour tous les composés examinés. La diphénylcarbazone a également été essayée comme indicateur. Les résultats obtenus ont été satisfaisants dans la plupart des cas, mais quelques anomalies ont été observées.

ZUSAMMENFASSUNG

Es werden einige Methoden zur Bestimmung von Thiolgruppen in organischen Proben, die nur 50 μg wiegen, beschrieben. Die jodometrischen Methoden waren nur begrenzt anwendbar, aber die mercurimetrische Methode von FRITZ UND PALMER, bei der Michlers Thioketon als Indikator dient, ergab ausgezeichnete Ergebnisse (± 0.5% absoluter Fehler) für alle untersuchten Verbindungen. Mit Diphenylcarbazon als Indikator war das Verfahren für die meisten Materialien befriedigend, jedoch wurden einige anormale Ergebnisse erhalten.

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SHORT COMMUNICATIONS

The equivalence point potential in redox titrations

Recently BRINKMAN[1] investigated the form of the equation which may be used to represent the potential at the equivalence point for a redox reaction of the general form

$$a\ \mathrm{Ox_1} + b\ \mathrm{Red_2} \rightleftarrows c\ \mathrm{Red_1} + d\ \mathrm{Ox_2} \tag{1}$$

which is valid, as is explicitly stated, only if both half-reactions involve the transfer of the same number of electrons. In this case the fundamental criterion for the equivalence point potential to be independent of the concentrations of any species which participate in the reaction is the relationship between *ad* and *bc*. The sole requirement for the equivalence point potential to be concentration independent is that $ad = bc$ instead of BISHOP's proposed requirement[2,3] that $a = c$ and $b = d$. In other words, even for inhomogeneous reactions where $a \neq c$ (and $b \neq d$) the equivalence point potential will be concentration independent if $ad = bc$.

However, it is of interest to consider a more general case, than does BRINKMAN, wherein the number of electrons for each half-reaction is different, in which case the redox reaction may be formulated as[2,3]

$$ax\ \mathrm{Ox_1} + by\ \mathrm{Red_2} \rightleftarrows cx\ \mathrm{Red_1} + dy\ \mathrm{Ox_2} \tag{2}$$

where $n_1x = n_2y$.

The Nernst expressions for the respective half-reactions are

$$E = E_1{}^{0\prime} - \frac{RT}{n_1F}\{c \ln [\mathrm{Red_1}] - a \ln [\mathrm{Ox_1}]\} \tag{3}$$

and

$$E = E_2{}^{0\prime} - \frac{RT}{n_2F}\{b \ln [\mathrm{Red_2}] - d \ln [\mathrm{Ox_2}]\} \tag{4}$$

where $E^{0\prime}$ represents the respective formal potentials, and R, T and F have their customary significance.

Throughout the titration, the concentrations of $\mathrm{Red_1}$ and $\mathrm{Ox_2}$ are interrelated by $[\mathrm{Ox_2}] = (dy/cx)[\mathrm{Red_1}]$, whereas *at, and only at* the equivalence point does $[\mathrm{Red_2}] = (by/ax)[\mathrm{Ox_1}]$. Substitution of these expressions into eqn. (4), results in

$$E^* = E_2{}^{0\prime} - \frac{RT}{n_2F}\{b \ln (by/ax) - d \ln (dy/cx) + b \ln [\mathrm{Ox_1}]^* - d \ln [\mathrm{Red_1}]^*\} \tag{5}$$

where E^* is the potential at the equivalence point and $[\mathrm{Red_1}]^*$ is the concentration of $\mathrm{Red_1}$ at the equivalence point.

Multiplication of eqn. (5) by an_2 and multiplication of eqn. (4) by bn_1, followed by addition of the two resulting equations and subsequent solution for E^* yields:

$$E^* = \frac{bn_1E_1^{0'} + an_2E_2^{0'}}{bn_1 + an_2} + \frac{RT}{(bn_1 + an_2)F}\{(ad - bc)\ln[\mathrm{Red}_1]^* + ad\ln(d/c) - ab\ln(b/a) + a(d - b)\ln(y/x)\} \quad (6)$$

which is very similar to the expression derived by BRINKMAN[1] except for the last term which may be written as $a(d - b)\ln(n_1/n_2)$.

It is thus readily seen that even when $x \neq y$ (*i.e.* $n_1 \neq n_2$), E^* is still concentration independent if $ad = bc$. But even if $b = d$ and $a = c$, E^* is dependent upon the value of n_1/n_2 since

$$E^* = \frac{byE_1^{0'} + axE_2^{0'}}{by + ax} \quad (7)$$

where use has been made of $n_1x = n_2y$.

However, if $a = b$ and $c = d$, then though the concentration term vanishes, E^* is nevertheless dependent upon the value of n_1/n_2:

$$E^* = \frac{n_1E_1^{0'} + n_2E_2^{0'}}{n_1 + n_2} + \frac{(d - b)RT}{(n_1 + n_2)F}\ln(n_1/n_2) \quad (8)$$

These conclusions are in agreement with those which may be made from the equations given by BARD AND SIMONSEN[4].

The degree of completeness of the redox reaction may be expressed by[1] $[\mathrm{Red}_1]^*/[\mathrm{Ox}_1]^*$, where the asterisk indicates the concentrations at the equivalence point. If one is however titrating Red_2 with Ox_1, it is somewhat more common[3,5] to represent the degree of completeness by $[\mathrm{Ox}_2]^*/[\mathrm{Red}_2]^*$.

The equilibrium constant for the reaction expressed by eqn. (2) is given by

$$K = \frac{[\mathrm{Red}_1]^{cx}[\mathrm{Ox}_2]^{dy}}{[\mathrm{Ox}_1]^{ax}[\mathrm{Red}_2]^{by}} \quad (9)$$

Now, at all times, $[\mathrm{Red}_1]/[\mathrm{Ox}_2] = cx/dy$ whereas only at the equivalence point does $[\mathrm{Red}_2]/[\mathrm{Ox}_2] = by/ax$. Substitution, by use of these expressions, of $[\mathrm{Ox}_2]^*$ and $[\mathrm{Red}_2]^*$, into eqn. (9), results in

$$\frac{[\mathrm{Red}_1]^{*cx+dy}}{[\mathrm{Ox}_1]^{*ax+by}} = [(by/ax)^b(cx/dy)^d]^y K \quad (10)$$

which means that in general the degree of completeness is concentration dependent unless $ax + by = cx + dy$. If $x = y$, only then does this requirement reduce to $a + b = c + d$ as given by BRINKMAN[1]. The same conclusion of course results if one investigates $[\mathrm{Ox}_1]^*/[\mathrm{Red}_2]^*$.

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Spectrophotometric determination of microgram quantities of serpentine, serpentinine and ajmalicine

SIDDIQUI AND SIDDIQUI[1,2] isolated a number of bases including serpentine, serpentinine, ajmalicine and ajmaline, from *Rauwolfia serpentina* Benth. These bases are of pharmacological importance but little has been done on the analysis of small amounts. Serpentine (50–100 μg) can be determined colorimetrically in mixtures with ajmaline and reserpine by reaction with methyl orange[3]; and ajmaline, ajmalicine, rescinnamine and asparagine can be determined photometrically with xanthhydrol after separation by solvent extraction and paper chromatography[4].

A simple spectrophotometric method recently described[5] for the determination of ajmaline in the presence of serpentine and ajmalicine, can be extended to the determination of serpentine, serpentinine and ajmalicine, all of which give a measurable yellow colour with concentrated nitric acid. When serpentine and serpentinine are present together, a chromatographic or electrophoretic separation is first effected and the bases are then separately estimated. No preliminary separation is required when ajmaline is present in combination with any of these alkaloids.

Apparatus and chemicals

A Unicam SP 600 spectrophotometer with 1-cm cells was used.

Alkaloid solutions. 0.1% solution of dried ajmaline; 0.05% solution of serpentine; 0.05% solution of serpentinine; 0.05% solution of ajmalicine. All the solutions were freshly prepared in ethanol.

Preparation of the calibration curves

Measure 10–100-μl aliquots, at 10-μl intervals, of serpentine or serpentinine or ajmalicine solution into 10-ml centrifuge cones with an "Agla" micrometer syringe. Evaporate to dryness under an infrared lamp or on a water bath. Pipet 5 ml of concentrated nitric acid and stir with a glass rod for 30 sec. Measure the absorbance at 365 mμ after 3 h in the case of serpentine and serpentinine against a blank of concentrated nitric acid. In the case of ajmalicine, measure the absorbance at 350 mμ after 8 h. The relationship between the absorbance and concentrations examined was found to be linear. Serpentine and serpentinine behave in a similar manner.

Procedures

(A) Serpentine or serpentinine or ajmalicine. Weigh 30–60 μg of the alkaloid on a microgram balance into a centrifuge cone; alternatively use a suitable ethanolic solution of the alkaloid and evaporate to dryness. Add 5 ml of concentrated nitric acid and continue as described for the preparation of calibration curves.

(B) Mixtures of ajmaline with serpentine or serpentinine or ajmalicine. Follow Procedure A and measure the absorbance after 3 h. Obtain the amount of serpentine or serpentinine by deducting the absorbance of ajmaline (after 3 h) from the absorbance due to the mixture of these alkaloids. The ajmaline is determined without interference from the other alkaloids as described previously[5]. In the case of ajmalicine, deduct the absorbance due to ajmaline at 350 mμ after 8 h.

(C) Mixtures of serpentine and serpentinine. Separate the two alkaloids by electrophoretic or chromatographic techniques. Cut the portions of the paper carrying

the spots into small pieces and soak in 5 ml of ethanol overnight. Take 4 ml of this solution, evaporate to dryness and treat the residue as in Procedure A.

(D) Unknown complexes, e.g. serpajmaline and ajmalexine. Prepare a solution of the complex in ethanol and subject an aliquot containing 80–120 µg of the complex to electrophoretic or chromatographic separation. Cut out the spots of serpentine and serpentinine and ajmalicine and treat as in Procedure A.

Results and discussion

On the addition of concentrated nitric acid to serpentine or serpentinine, a deep yellow colour develops. With 100-µg samples, the absorbance at 365 mµ reached a maximum after 3 h and remained constant; with smaller amounts (50 µg), the absorbance attained a constant value after 1 h. Accordingly, the absorbance was always measured after 3 h. The absorbance maximum occurred at 365 mµ and was unaffected by changes in the concentration of serpentine or serpentinine.

With ajmalicine, the maximum absorbance was found at 350 mµ (see Fig. 3 of ref. 5). Again, the absorbance increased with time, becoming constant only after 8 h with 100-µg amounts, but after 2.5 h with 50-µg amounts.

In contrast to the other alkaloids mentioned, ajmaline gave a red coloration with concentrated nitric acid which faded quickly leaving a light yellowish residual colour; the maximum absorbance of ajmaline after 3 h occurred at 340 mµ. Since the maxima in the case of serpentine (see Fig. 2 of ref. 5) and serpentinine occurred at 365 mµ, the absorbance of ajmaline was also measured at 365 mµ after 3 h. Table I shows the absorbance due to different amounts of ajmaline at this wavelength and the results obtained for serpentine when increasing amounts of ajmaline were added to 50 µg of serpentine and the absorbance was measured at 365 mµ after 3 h. The absorbances due to ajmaline and serpentine or serpentinine proved to be additive and serpentine or serpentinine could therefore be determined by subtracting the absorbance due to ajmaline from the total absorbance. Ajmaline alone was determined separately in all cases by the previous method[5]. With mixtures of ajmaline and ajmalicine, the absorbances were again additive; the absorbance of ajmalicine at 350 mµ became constant only after 8 h and the contribution due to ajmaline was therefore also measured under these conditions. The results obtained for ajmaline–ajmalicine mixtures were similar to those shown in Table I.

TABLE I

DETERMINATION OF AJMALINE AND SERPENTINE

Ajmaline present (µg)	*Ajmaline absorbance*[a] *(a)*	*Serpentine present (µg)*	*Absorbance of mixture (b)*	*Serpentine found from (b−a)*	*Error (µg)*
—	—	50	0.250	50.0	0.0
10	0.055	50	0.310	51.0	+1.0
20	0.090	50	0.345	51.0	+1.0
30	0.125	50	0.372	49.5	−0.5
40	0.160	50	0.410	50.0	0.0
50	0.200	50	0.450	50.0	0.0

[a] Absorbance at 365 mµ after 3 h.

Results for the determination of serpentine and serpentinine after chromatographic or electrophoretic separation are shown in Table II. To check the method for the analysis of materials such as ajmalexine and serpajmaline, synthetic mixtures of ajmaline, serpentine and serpentinine and of ajmaline and ajmalicine were prepared; with a mixture of 35.0 μg of ajmaline, 49.0 μg of serpentine and 13.6 μg of serpentinine, the amounts found were 34.5, 49.5 and 13.75 μg respectively.

TABLE II

DETERMINATION OF SERPENTINE AND SERPENTININE

	Amount in spot (μg)	*Absorbance*	*Amount found*[a] *(μg)*	*Error (μg)*
Serpentine	50	0.20	50.0	Nil
	50	0.195	49.3	−0.7
	30	0.115	29.38	−0.62
	30	0.119	30.6	+0.6
	25	0.105	25.0	Nil
Serpentinine	80	0.319	80.0	Nil
	80	0.315	79.0	−1.0
	40	0.155	39.38	−0.62
	40	0.459	40.0	Nil
	30	0.115	30.0	−1.0
	30	0.12	30.0	Nil

[a] Corrected to 5 ml.

The development of the yellow colour with serpentinine, serpentine and ajmalicine with concentrated nitric acid is not specific for these alkaloids; other derivatives of ajmaline react in the same manner if the reactants are allowed to stand for several hours. However, when the mixture of the alkaloids is separated chromatographically, each alkaloid can be determined without interference. The method has the added advantage of being rapid, accurate and simple, compared to some available methods. There is no effect of light or small variations in temperature on the development of colour and no rigid control of the experimental conditions is necessary.

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High-precision titrimetry of boric acid: Some calculations and measurements of inflection points

To complete previous studies on the high-precision analysis of aqueous boric acid solutions[1,2], some additional parameters of the system used for the analysis have been examined.

In the earlier method a solution of 0.015 *M* boric acid and 0.26 *M* mannitol was titrated with a 0.1 *M* sodium hydroxide solution. The base used was standardized against several primary standard substances. The end-point was detected by the differential potentiometry of stepwise additions of the base. The results of the present work are described below.

(*1*) The pK_A of the above reaction medium was calculated, by the general formula developed by LINGANE[3], from the pH values measured at 25° in the middle sections of the titration curves. The value of 5.23 found was the average of the results calculated for 3 complete titration curves.

(*2*) The molarity of the mannitol in the same medium was varied from 0.05 to 0.75, which represents 3.5 to 50 times the molarity of the boric acid titrated. The pK_A values calculated from pH measurements at the start of the titrations are given in Table I.

TABLE I

Molarity of mannitol	*0.05*	*0.13*	*0.26*	*0.40*	*0.53*	*0.64*	*0.75*	*Excess*
pK_A	6.5	5.8	5.2	4.9	4.7	4.5	4.4	4.4

As a result of this change in concentration of mannitol, the pH value of the end-point of the titration was also displaced. For the same quantity of boric acid present, the pH of the end-point with 0.26 *M* mannitol was found at 8.6, whilst this pH for a solution saturated with mannitol was about 8.0.

(*3*) The formulae given by MEITES AND GOLDMAN[4,5] for the calculation of the location of the end-points of acid–base titrations were used for this case.

The value $0.65 \cdot 10^{-5}$ for K_A of the boric acid–mannitol complex was calculated and used in the above-mentioned formula. It was found[6] that under the conditions used the inflection point of the titration curve coincided with the theoretical equivalence point to better than 0.01%.

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Spurious X-ray diffraction patterns of orthovanillic acid caused by grinding at room temperature

Grinding to reduce the particle size of a crystalline solid is usually necessary in order to produce reliable DEBYE–SCHERRER X-ray powder patterns. It has been pointed out[1-3] that, due to the possibilities of line broadening, prolonged grinding should be avoided. The possibility that grinding may alter the structure of crystals[4,5] has not received much attention. This note illustrates the variations in the diffraction pattern of an organic compound which were caused by mild grinding and also describes a remedial procedure.

X-Ray diffraction patterns of orthovanillic acid (m.p. 149–150° recrystallized from water) were obtained with a Norelco X-ray diffraction unit using Fe-filtered Co radiation. Powder samples were placed in glass tubes of 0.2-mm bore mounted in 114.6-mm DEBYE–SCHERRER cameras and exposed for approximately 10 h.

The effect of grinding on the powder patterns is illustrated in Fig. 1a to 1e. Initially moderate manual grinding at room temperature gave samples which

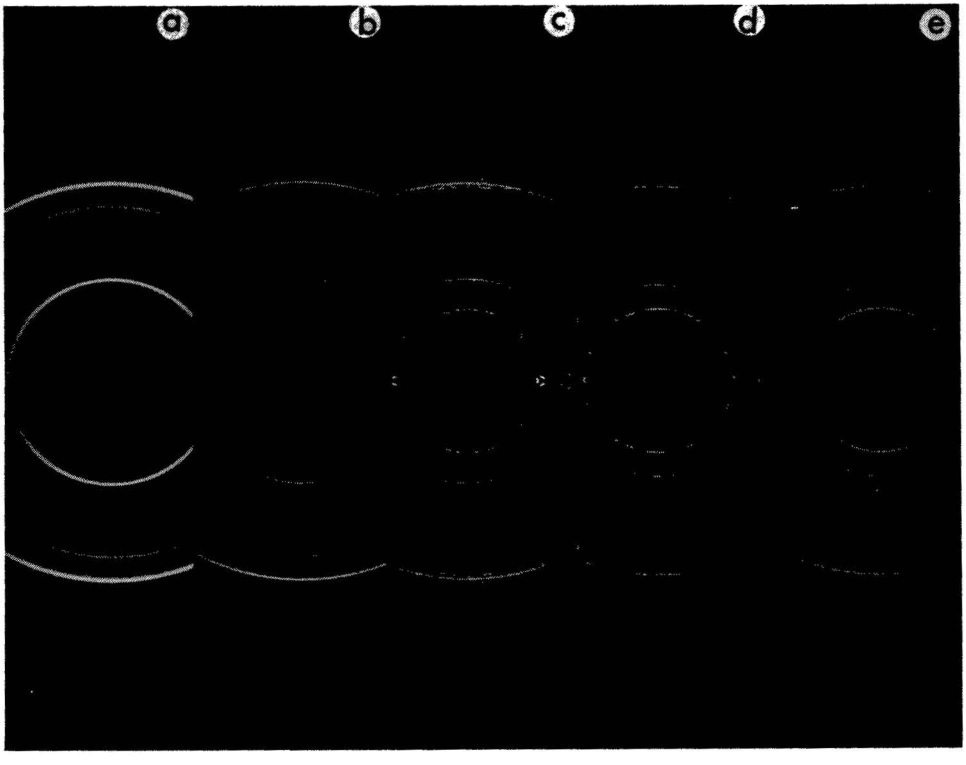

Fig. 1. X-ray powder diffraction films representing specimen preparation by different grinding procedures applied to orthovanillic acid. Fe-filtered Co radiation, 114.7-mm camera. (a) Moderate grinding-room temperature; (b) Moderate grinding-room temperature; (c) Moderate grinding-room temperature; (d) Minimum grinding-room temperature; (e) Moderate grinding-cold temperature (Dry Ice in alcohol).

produced X-ray patterns consisting of smooth diffuse lines with varying intensities and spacings (Fig. 1a and b). Milder grinding at room temperatures produced patterns with spotty lines (Fig. 1d). A slight increase in grinding produced patterns with diffuse unbroken lines as well as spotty ones (Fig. 1c). The latter pattern was a composite of that shown in Fig. 1a and d. In all of these experiments, the samples were passed through a 300-mesh sieve and appeared to be homogeneous when examined under a binocular microscope. From these results it is concluded that grinding of orthovanillic acid at room temperature had altered the material from that producing the pattern shown in Fig. 1d to that giving rise to the pattern in Fig. 1b. Furthermore, in these experiments exemplified by Fig. 1c and in other unreported attempts at cautious grinding at room temperature, it was impossible to eliminate the undesirable spottiness in the pattern without changing the positions and intensities of the lines.

Further experimentation showed that cold grinding of orthovanillic acid resulted in satisfactory X-ray diffraction patterns with smooth narrow lines (Fig. 1e) having d-spacings and intensities comparable to those in Fig. 1d. Moreover, it was found that extended or vigorous grinding in the cold did not alter the diffraction pattern. The difference in the powder patterns obtained by grinding in the cold and at room temperature is shown in Table I.

The procedure used most successfully was as follows. A mortar containing the organic material and a pestle was cooled for 5 min by a mixture of Dry Ice and

TABLE I

X-RAY DIFFRACTION POWDER PATTERNS FROM ORTHOVANILLIC ACID GROUND AT ROOM TEMPERATURE AND IN THE COLD

Cold (film no. 5)		*Room temperature (film no. 2)*	
I/I_1[a]	*d*	I/I_1	*d*
		1	14.05
10	8.97		
v	7.29		
9	6.94	1	6.92
v	6.29	9	6.29
7	5.90		
1.5	5.64	3	5.64
4.5	5.46		
4.5	4.99		
v	4.64		
4	4.33		
4.5	3.97		
4.5	3.86	0.5	3.86
		6	3.70
4.5	3.63		
1.5	3.56	4	3.56
1.5	3.46		
8	3.34		
v	3.27	10	3.27
6	3.21		
1	3.14	0.5	3.14
v	3.09		
5	2.99	0.5	2.99

[a] Relative intensities estimated by visual inspection. v = very faint or just visible.

ethanol. With a minimum of grinding, the sample was powdered to a particle size just sufficiently small to enter a 0.2-mm glass capillary. The ground material was then transferred to a desiccator and allowed to reach room temperature. The sample thus prepared gave a powder photograph consisting entirely of spotty lines which was used as a guide for the final grinding operation. Further gentle grinding in the cold was continued until the powder photograph consisted of thin solid lines having identical d-spacings as the spotty lines. In this way broad diffuse lines as well as spotty lines were avoided.

The above variations in diffraction patterns, whatever the cause, may be the source of serious errors in the identification of unknowns because the Hanawalt system uses the three or four strongest lines for indexing. The reliability of some of the X-ray powder patterns of organic compounds in the analytical literature is questionable, particularly where a mixture of spotty and diffuse lines similar to those encountered in this investigation have been reported[6]. It would appear that greater care should be taken regarding the grinding procedure used for other analytical techniques as well as for X-ray diffraction.

The results presented here suggest that gross errors can be avoided and more reliable results can be obtained by (*1*) using a spotty pattern of slightly ground material as a guide to determine whether powder patterns with solid lines represent unaltered material, and (*2*) using a cold grinding procedure in order to prevent changes in diffraction patterns.

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N. M. MILES

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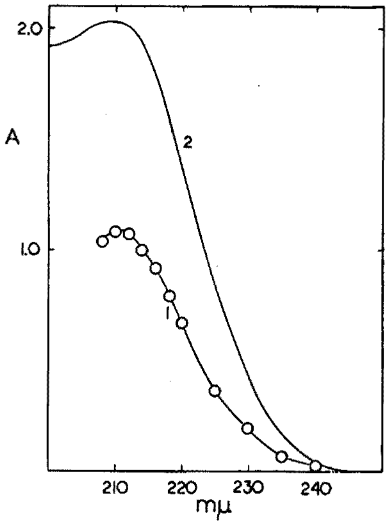
Anal. Chim. Acta, 32 (1965) 223–225

Spectrophotometric determination of high-molecular weight polyacrylamides and maleic anhydride copolymers

For the determination of small amounts of polymers in solution, methods employing radioactive tracer isotopes are suitable but these are often time-consuming and impractical. In a recent publication[1] it was briefly indicated that polyacrylamide (PAM) absorbs in the ultraviolet wavelength range. The present communication reports additional findings including the dependence of ultraviolet absorption on the molecular weight of PAM, and an ultraviolet spectrophotometric determination of vinyl acetate–maleic anhydride copolymers. This technique may be extended to other polymers containing side-chain carbonyl groups.



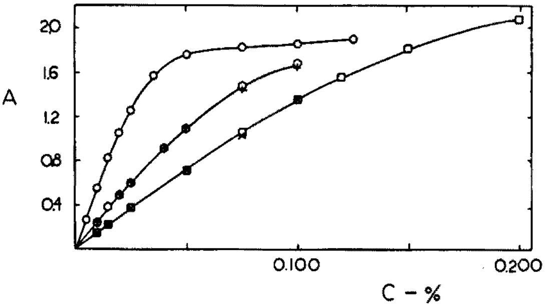


Fig. 1. Absorption spectra. Curve 1 : 0.050% aqueous solution of PAM ($3.0 \cdot 10^6$ average molecular wt.) with a Beckman DU spectrophotometer. Curve 2: 0.100% aqueous solution of PAM ($1.0 \cdot 10^6$ average molecular wt.) with a Cary Recording spectrophotometer.

Fig. 2. Absorbance *vs.* concentration curves. + PAM, $5.0 \cdot 10^5$ average molecular weight (212 mμ); ◯ PAM, $6.0 \cdot 10^6$ average molecular weight (212 mμ); × PAM, $5.0 \cdot 10^5$ average molecular weight (220 mμ); □ PAM, $6.0 \cdot 10^6$ average molecular weight (220 mμ); ○ vinyl acetate–maleic anhydride copolymer (212 mμ).

Ultraviolet absorption curves obtained with aqueous solutions of PAM ($1.0 \cdot 10^6$ and $3.0 \cdot 10^6$ average molecular weight[2]) are shown in Fig. 1. The maximum absorbance occurs at 208–212 mμ. Vinyl acetate–maleic anhydride copolymers (*e.g.* Lytron 886, $2.0 \cdot 10^5$ average molecular weight, Monsanto) in aqueous solutions also show an absorption maximum at 210–212 mμ. The plots of absorbance *vs.* concentration for these polymers are given in Fig. 2. It can be seen that at very low concentrations, approximately below 0.025%, these polymers behave in accordance with Beer's law, but standardization curves are required at higher polymer concentrations. It can be observed that the absorbance of PAM-s is independent of the molecular weight in the $5.0 \cdot 10^5$ to $6.0 \cdot 10^6$ molecular weight region. This conclusion has also been tested with PAM-s of $1.0 \cdot 10^6$ and $3.0 \cdot 10^6$ molecular weights[2].

From these experimental data the values of the molar absorptivities have been calculated at the lowest concentrations studied. For easier comparison the molecular weights of the corresponding monomers were used in the calculations. The molar absorptivities are as follows:

PAM, $5.0 \cdot 10^5$–$6.0 \cdot 10^6$ average molecular weight, at 212 mμ: $\varepsilon = 183$; PAM, $5.0 \cdot$

10^5–$6.0 \cdot 10^6$ average molecular weight, at 220 mμ: $\varepsilon = 112$; Lytron 886, $2.0 \cdot 10^5$ average molecular weight, at 212 mμ: $\varepsilon = 1990$.

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1 L. JANKOVICS, *J. Polymer Sci. Part B. Polymer Letters*, 2 (1964) 247.
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(Received November 28th, 1964)

BOOK REVIEWS

J. N. BUTLER, *Solubility and pH Calculations*, Addison-Wesley Publishing Company Inc., Reading, Mass., 1964, viii + 104 pp., price: hardbound \$2.95; paperbound \$1.75.

The reviewer recently had the pleasure of recommending Dr. BUTLER's book *Ionic Equilibrium* to readers of this Journal. The present book uses the same approach as that book for solving problems associated with ionic equilibria, and is presented in the same lucid way. Attention is directed mainly to worked examples of problems associated with solubility and with weak acids and bases. The book has been written for the student who finds difficulty with the mathematics of simple ionic equilibrium calculations, but who has some knowledge of the concept of chemical equilibrium. In its cheaper paper-back edition, it is bound to appeal widely to students of elementary chemistry who find the problems of ionic equilibrium altogether too mysterious for calculation.

W. I. STEPHEN (Birmingham)

Proceedings of the Conference on Methods of Preparing and Storing Marked Molecules, Brussels, 1963, Edited by J. SIRCHIS, EUR 1625e, Information and Documentation Centre, European Atomic Energy Community, Brussels, 1964, xxiii + 1359 pp.

These Proceedings comprise two parts. Part I consists of the individual papers and the discussions in the original language, while an English translation of these texts is provided in Part II. A collection of papers of this sort necessitates coverage of certain specialised topics but many of the techniques and principles involved are more generally applied. New approaches are given for the introduction of isotopes of H, C, P, I, S and O into a wide range of organic molecules, particularly those of biological importance. A variety of problems concerning the production, storing and use of radioactive isotopes are discussed.

J. S. BRIMACOMBE (Birmingham)

ERRATUM

Erratum. W. W. Wendlandt, S. Iftikar Ali and C. H. Stembridge, *Anal. Chim. Acta,* 31 (1964) 501–508.

Some legends to the Figures were omitted in the above paper. The legends are:

Fig. 2. DTA curves of metal cupferrates (argon). (A) $Cd(Cup)_2$; (B) $Hg(Cup)_2$; (C) $Ca(Cup)_2 \cdot 2H_2O$; (D) $Ba(Cup)_2 \cdot 3H_2O$; (E) $Sr(Cup)_2 \cdot 2H_2O$; (F) $Mg(Cup)_2$.

Fig. 3. DTA curves of metal cupferrates (argon). (A) $Al(Cup)_3$; (B) $Fe(Cup)_3$; (C) $Ce(Cup)_3$; (D) $La(Cup)_3$; (E) $Nd(Cup)_3$.

Fig. 4. DTA curves of cupferron and metal cupferrates (vacuum). (A) Cupferron; (B) $Cu(Cup)_2$; (C) $Fe(Cup)_3$; (D) $Al(Cup)_3$; (E) $La(Cup)_3$; (F) $Nd(Cup)_3$.

ANNOUNCEMENT

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The first Middle Atlantic Regional Meeting will be held at the Sheraton Hotel in Philadelphia on February 3–4, 1966. The Local Sections co-sponsoring this meeting are: Delaware, Lehigh Valley, Monmouth County, New York, New Jersey, Philadelphia, Princeton, Southeastern Pennsylvania, South Jersey and Trenton. Members of the American Chemical Society are invited to present papers in the following fields: Analytical Chemistry, Chemical Education, Industrial and Engineering Chemistry (including Chemical Marketing and Economics), Inorganic Chemistry, Medicinal and Biochemistry, Organic Chemistry, Petroleum Chemistry, Physical Chemistry and Polymer Chemistry.

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The ACS regulations require that (*1*) at least one author of a paper be a member of the ACS and (*2*) the paper be presented by a chemist or chemical engineer residing in the U.S.A. Such papers may later be submitted for publication in ACS Journals or presentation at National Meetings.

For further information, contact: Dr. Walter Clavan, General Chairman, First Middle Atlantic Regional Meeting, Pennsalt Chemicals Corporation, King of Prussia, Pennsylvania 19406, or the above office.

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G. H. Bannister, R. C. Burnett and J. R. Murray, *J. Nucl. Mater.*, *2* (1960) 51.

Books:
L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1955, p. 445.

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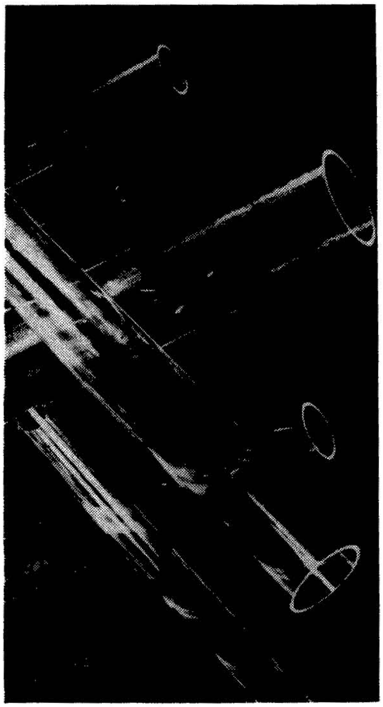

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THE BACTERIAL CELL WALL

by M. R. J. Salton, Professor of Microbiology, School of Biological Sciences, University of New South Wales, Australia

THE BACTERIAL CELL WALL deals with all aspects of the structure, function and nature of microbial cell walls. It begins with a detailed discussion of the anatomy of the bacterial surface, and an attempt is made to place this relatively new information into perspective with the current status of our knowledge of cell structure in other organisms. The functions, nature and inter-relationships of the principal surface components, capsules, walls and membranes are discussed; methods of cell disintegration for the isolation of bacterial walls are outlined and critically assessed; procedures and technical details of the steps used in the separation of cell walls and surface membranes from other cell components are given. All information on the general chemical composition of bacterial cell walls has been collected together with special emphasis on the amino acid, amino sugar and sugar compounds of the walls.

Contents

1. Introduction. The anatomy of the bacterial surface. 2. Isolation of bacterial cell walls. 3. Electron microscopy of isolated walls. 4. Physico-chemical properties and chemical composition of walls. 5. Structure of cell-wall gyclosaminopeptides (mucopeptides) and their sensitivity to enzymatic degradation. 6. The occurrence and structure of teichoic acids. 7. Cell-wall antigens and bacteriophage receptors. 8. Biochemistry of the bacterial cell wall. 9. On looking back. Index.

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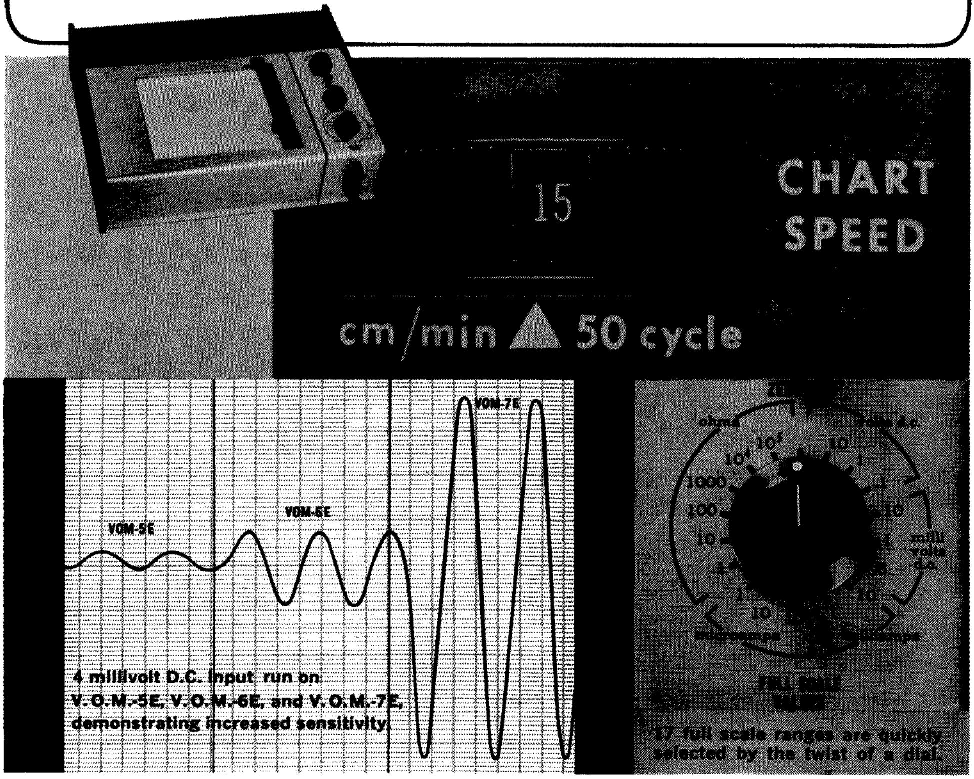

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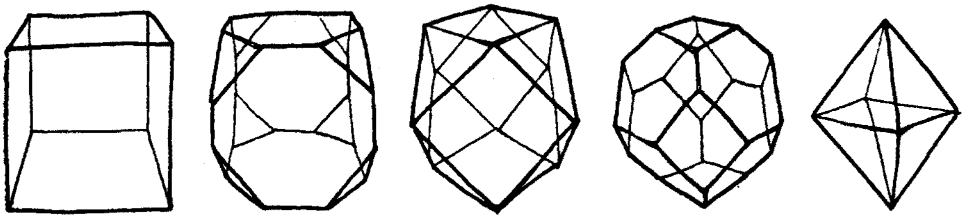

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